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CHEMISTRY
for
ELECTROPLATERS

by

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FOREWORD

THE development of plating of metals as a chemical and electrical process (rather than as a mechanical operation such as the making of Sheffield Plate) has been a major achievement of the metallurgical industries during the past one hundred years. Although electroplating involves some of the most complicated theoretical aspects of both chemistry and electrical physics, yet there are few indeed who have made the attempt to operate such processes based on theoretical background and understanding. Fortunate it is that most of the industrial work in this field may be carried on without comprehension of the physical and chemical mechanisms involved.

There has developed an art rather than a science in most electroplating plants; and a large amount of the best work is done by those who have a feeling and skill for it rather than an understanding of the laws governing their work. Nevertheless, much of the background required for the understanding of the principles of electroplating is in the relatively simpler fields of chemistry, and it has been the attempt of the author to present the theory in a way which would allow those who work with the processes to become more familiar with the fundamentals of the science behind their art, so that by better understanding they can do better work.

Dr. Young is well qualified to know the needs of men working in the electroplating industries and also their backgrounds which will be the basis for their assimilation of this material. He has had considerable practical experience as consultant to many of the large companies using electroplating in the solution

of their problems and the furtherance of electroplating technology. He has also, by reason of his years of professorship and the direction of research in Electro-Chemical Technology at the Polytechnic Institute of Brooklyn, and at other schools, acquired the ability to present these scientific facts and theories in a readily understandable manner.

It appears that he has done so, and those who seriously study the following pages and make a real effort to solve the numerous illustrative problems will appreciate the facts presented as of real help in their work, as well as enjoy the interesting method of presentation used.

DONALD F. OTHMER
Polytechnic Institute of Brooklyn

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Dedicated to the Plater who has Enough Courage to Study after a Long Tiring Day over Troublesome Plating Tanks.

CHAPTER I

Chemistry and Chemical Change; Element, Compound, Mixture; Oxygen

THIS book is designed to give the electroplater a fundamental nowledge of the theories underlying chemistry so that he may e able to apply the same theories, producing better work in the lant. It is impossible to design a study in which the student ill have nothing to do except read chapters for a few times nd the results pour forth. It is absolutely essential that the tudent does his part.

The following chapters contain the fundamental laws of iemistry. Here the student is introduced to the behavior of ie elements. One may think that a study of chemistry for ectroplaters is a waste of time, but this is not the case. The undamental laws of chemistry are the foundation for electro-iemistry and in order to cope with the many problems which rise in electroplating, one must be well grounded in the study f the elements. As an example, if one desires to analyze the ickel sulfate in a nickel plating solution, it is essential that one btains a standardized sodium cyanide solution. How are we o determine the method of standardization of this sodium yanide? This and many other questions can be answered only y a scientific study of chemistry.

Chemistry is a study of the elements. Our universe is made p of only ninety-two elements. Wherever we go and whatever

we see, the material upon which our eyes fall can be subdivided into these building blocks of nature. For instance, water is made up of two elements, hydrogen and oxygen. Sulfuric acid is made up of three elements, hydrogen, sulfur and oxygen. It makes no difference whether one picks up wood, concrete, steel, cotton, or any other material, one can always break these down into their constituents which are the elements. Chemistry deals with the composition and changes in composition of substances. It is also concerned with their properties and their energy relations. In order to study chemistry from a scientific point of view, it is necessary first to classify the elements according to their fields and learn their general properties. In this way, a broad field can be covered in a rather limited time. In our study we are particularly interested in those elements which enter the field of electroplating, and throughout this book, emphasis will be placed upon these elements. In other words, we shall study chemistry from the point of view of the electroplaters.

When a chemical change occurs, what happens? All electroplaters are familiar with the corrosion of metals. If this is analyzed, it will be seen that it is due to the union of the metal with another element or compound. For instance, when iron is left in the open, it rusts. When iron rusts, it is transformed and is no longer iron. Therefore, we have a chemical change. Whenever a fire is built, the coal which is burned is transformed into ashes and gases. Again a chemical change has taken place. In the electroplating shop, chemical change takes place when a piece of metal is cleaned from rust or scale. The whole is dipped into an acid solution and the scale is dissolved. Here the scale changes from an insoluble material to one that is soluble. If silver is deposited from a silver cyanide solution, using iron anodes, the silver cyanide is transformed to silver. This again is a chemical change.

If a chemical change has taken place, one can rest assured

that the original products have been transformed or changed into another product. Thus, if a match is lighted and burned, the results are (1) smoke or gases liberated, and (2) a black mass of carbon left behind. These materials are quite different from the original phosphorus and wood. It can readily be seen that the final products are quite different from the original products. Again, if silver is deposited from a silver cyanide strike, we know that metallic silver is quite different from the original compound, silver cyanide. It may be said that in every chemical change one or more materials seem to disappear and one or more new substances are formed. As a general rule, heat is given off or taken in and light is often produced in a chemical change.

How does the chemist recognize different materials? Compounds and elements have faces the same as humans. How do we tell our friends apart? One has brown hair, blue eyes and weighs 175 pounds, while another has black hair, brown eyes and weighs 145 pounds. There is no trouble in telling such people apart. In the same way, the chemist can tell the difference between two compounds. For instance, iron rust is reddish-brown and crumbles very easily. On the other hand, iron is of steel-gray color and very hard. Any person can recognize these differences. Aside from these characteristics which are known as physical properties, the chemist recognizes materials by their actions, or chemical properties. Thus, iron rusts and forms a reddish-brown material, whereas gold does not. For this reason, steel and other materials are often covered with gold for protection. In identifying materials, one should never rely on one test alone. Many properties should be used to identify a substance.

If a chemical change has taken place, new materials have formed. That is, the materials produced will not have the same properties as the former substance had. Thus, iron rusts and forms, as has been pointed out, a reddish-brown material which

crumbles very easily. This material is quite different from iron because it has (1) a different color, (2) is lighter in weight, (3) crumbles under pressure, (4) is not attracted to a magnet. Therefore, we can say that the original iron has disappeared and a new material has formed in its place. We recognize the change which has taken place by observing that the initial material is quite different from the final product.

All matter must be accounted for. It is impossible to create or destroy matter. True, one may change the form of materials and render them impossible for use from the point of view of man, but they are never erased or destroyed in the chemical sense. Perhaps, an explanation here would help. A piece of wood may be burned but no matter has been destroyed. The gases which are released plus the ashes are equal to the wood plus the air which aided the burning. Therefore, a building which is burned is destroyed from the point of view of using it for storing purposes, but chemically speaking, a chemical reaction has taken place and the wood has been transformed into other substances. When a chemical experiment is performed, the materials entering the reaction are always equal to the materials formed by the same reaction. This is the law of conservation of matter.

A substance which consists of uniform parts is said to be homogeneous. A substance which is composed of unlike parts is said to be heterogeneous. For instance, an example of the first is common salt. If a sample of common salt is examined under the microscope, one finds that it contains a large number of small cubes. These cubes may vary in size but they all have the same color and same general substance. No matter how high we magnify these parts, only one structure can be found, namely, salt. If dirty salt is examined, we can find substances of at least two different types, namely, salt and materials which are not salt. With the aid of a microscope it is possible to see

these particles and if tweezers are used one can separate the salt from the dirt by merely picking out the salt crystals and leaving behind the dirt. Another example of this would be a mixture of iron and sulfur. Iron, in the finely divided state, is black while sulfur is yellow. We can also separate the two substances by using tweezers or a magnet which will attract the iron and not the sulfur. We can also separate them by pouring carbon disulfide over the mixture. The carbon disulfide dissolves the sulfur and leaves behind the iron. On evaporating the carbon disulfide, yellow sulfur is obtained. A mixture contains two or more distinct ingredients or compounds which retain their own properties and can be separated by physical means, whereas the properties of a compound differ from those of its ingredients and it cannot be separated into ingredients by simple, physical means. In the introduction, the fact was mentioned that in our universe there are ninety-two elements. When these elements are united chemically, and not merely mixed together, chemical compounds are obtained. As has been pointed out, water is a chemical compound, being composed of two gases, hydrogen and oxygen. This can be proven by decomposing water by electrolysis of the solution. If an apparatus is set up, as shown in figure I, and current passed through the water, it will be noticed that the water decomposes and on each electrode a gas is liberated. It will also be observed that the positive side or anode will contain half the amount of gas as the negative side or cathode. If a test for these gases is made, it will be found that the gas which was released at the positive side is oxygen, and the gas that is released at the negative side is hydrogen. From this experiment, it can be seen that water has been broken up into its constituents: hydrogen and oxygen.

If mercuric oxide is examined, it is found to be a red powder. If further examined under a microscope, it will be seen that the material is homogeneous, that is, every part is similar to the

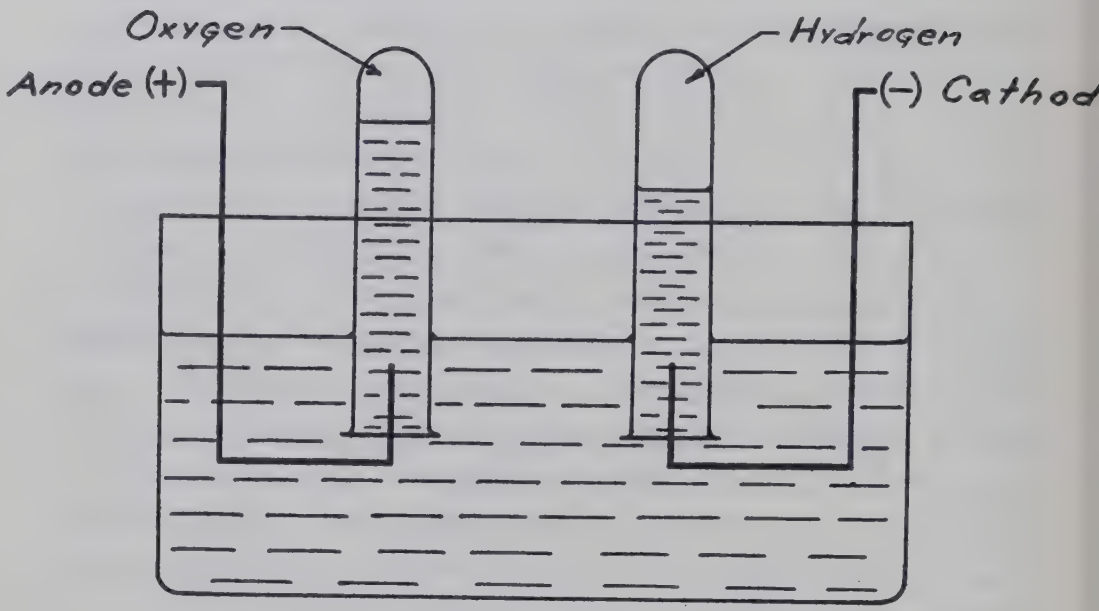

FIG. I

rest. Now if some of this material is placed in a test tube and heated, it will be noted that the red powder becomes dark. If a glowing splint is introduced into the mouth of the test tube, it bursts at once into flame. This indicates that oxygen is being liberated. On examining closely the tube which contains the red powder, it will be noted that in the cooler or upper part of the tube little drops of mercury have collected. If the heating was carried out long enough, all the red powder will have disappeared, liberating oxygen as a gas and mercury or quicksilver as a liquid. This experiment shows that the red oxide of mercury is composed of two elements: mercury and oxygen. Any substance which can be decomposed into two or more other substances is called a chemical compound.

An element cannot be decomposed into simpler substances. One thing should be mentioned at this point and that is that if

two materials or elements are in chemical combination, both lose their chemical faces or identity and assume new faces or properties. Thus, water is a colorless, odorless, tasteless liquid which freezes at 0°C and which will dissolve many materials. This compound, as we have said, is composed of two gases, hydrogen and oxygen. Hydrogen is a colorless, odorless, tasteless gas which is the lightest element in the world. Oxygen is a colorless, odorless, tasteless gas, sixteen times heavier than hydrogen. There is no similarity whatever between water, hydrogen, or oxygen. The same is true of mercuric oxide. This material is composed of two elements, mercury and oxygen. Mercury is a silver-colored liquid metal, whereas oxygen is a gas which has just been described. These two elements combine to give a compound which is a red powder. Elements form compounds.

In the preceding paragraphs, the breaking down of two compounds and obtaining their constituent elements were discussed. Now, we shall reverse this process by taking two elements and making a compound. If a small amount of sulfur is placed in a mortar or grinding dish and then some mercury or quicksilver is introduced, and the two elements are ground together, it will be found that after stirring a few moments, the sulfur loses its beautiful yellow color and begins to assume a dark-gray to black color. At the same time, it will be observed also that the mercury or quicksilver disappears. On further investigation, it will be noted that a new compound, which is quite unlike the mercury or the sulfur, has been formed. This compound is mercuric sulfide which is a black powder, wholly different from either the mercury or the sulfur. Again the properties of mercuric sulfide are very different from the properties of mercury or sulfur. Mercuric sulfide has a group of characteristic properties which distinguish it from other compounds or elements.

The chemist desires, many times, to indicate a chemical

changes. He would like to put this in a very condensed form. For instance, we can represent the change of the red mercuric oxide to mercury and oxygen by merely writing: Mercuric Oxide = Mercury + Oxygen.

(108) (100) (8)

It will be noted that under mercuric oxide appears the number (108), under mercury appears (100), and under oxygen appears (8). These are the molecular and atomic weights respectively, of the compound and the two elements. This will be further explained in a subsequent chapter. It will be noted that 108 parts of mercuric oxide produce 100 parts of mercury and 8 parts of oxygen. If the mercuric oxide for the experiment is obtained from South America, France, Germany, Spain, Africa, or India, it will always be found that on decomposing the mercuric oxide $\frac{100}{108}$, or 92.6%, of the weight used results in mercury and $\frac{8}{108}$, or 7.4%, of the weight gives oxygen. This compound always decomposes in this ratio.

The union of iron and sulfur, giving iron sulfide, may be represented as Iron + Sulfur = Iron Sulfide.

(55.84) (32) (87.84)

From this, it can be seen that 55.84 parts of iron unite with 32 parts of sulfur to give 87.84 parts of iron sulfide. Now the composition of iron sulfide is $\frac{55.84}{87.84}$, or 63.6%, iron and $\frac{32}{87.84}$, or 36.4%, sulfur. It will be noted that if the percentage of iron and the percentage of sulfur, namely 63.6 and 36.4, are added together, the result is 100%, which means that iron sulfide is composed only of iron and sulfur in this ratio and nothing else. This and many other compounds have been checked by

quantitative analysis and each time the prediction has come true regardless of where the compound or elements came from, provided they were chemically pure. Therefore, we may conclude that every pure compound has a definite composition by weight. This is known as the law of definite composition.

The big difference between a mixture and a compound lies in the fact that a compound can be separated into its ingredients by chemical means only whereas the ingredients of a mixture can be separated by simple, physical means. If a substance can be separated into its ingredients by mechanical means it is a mixture. For instance, sand and salt can be separated by using tweezers to pick the small crystals of sand and leave behind the crystals of salt. This would be a trying undertaking, but it could be accomplished if necessary, but it would be impossible to separate water into its components by mechanical means. In this manner, we can generally distinguish between a compound and a mixture.

A mixture can often be separated because the materials which make up the mixture retain their common faces or properties. For instance, if salt and sand are mixed the salt has not lost any of its properties, neither has the sand. It is common knowledge that sand is insoluble in water, whereas salt will dissolve very readily in this liquid. Therefore, if this mixture is put into water and agitated, it will be found that the salt dissolves, leaving behind the sand. If the water is poured off, the aqueous solution will contain the salt and the sand be left behind. Now, if the water is evaporated, the salt will be recovered. Thus by an ordinary mechanical operation it is possible to separate the salt from the sand. A similar illustration was used earlier. In that instance, sulfur was dissolved by carbon disulfide and then recovered as above.

Although there are 92 elements, only 25 of these are common. If the earth's crust is analyzed, it will be seen that oxygen

is the most abundant element, with silicon next, and then aluminum which is followed by iron, etc. Contrary to common belief, there is more aluminum than iron. One would think from this that aluminum and its alloys are more frequently used than iron and its alloys. Aluminum has not been used more on account of the high cost of its recovery. We shall learn more about this interesting element later on.

The elements are divided into two classes: metals and non-metals. Iron, aluminum, copper, gold, and silver, etc., are good examples of the first group. The electroplater is quite interested in some of these as he uses them every day in his plant. The non-metals are oxygen, hydrogen, nitrogen, sulfur, carbon, phosphorus, etc. These are also used by the electroplater indirectly. For instance, in a nickel bath which consists of nickel sulfate made up of nickel, sulfur, and oxygen, the electroplater uses the sulfur and oxygen in order to deposit the nickel.

The number of compounds which can be produced from the 92 elements is tremendous. At present, over one half million compounds are known and our laboratories are turning out new ones every day. It would be impossible for anyone to study every one of these compounds intelligently. We are rather fortunate, though, in that only a limited number of these compounds is important for the electroplater and many of these can be divided into groups which are similar. By studying one group, it is possible to become familiar with the many compounds which make up this group.

Earlier, it was stated that our universe is composed of 92 elements. We shall study 30 or 40 of the most important ones. The first to be studied is oxygen. This material has been mentioned several times before. It will be recalled that oxygen was obtained from red oxide of mercury. It was also mentioned as a component of water. The electroplater knows it as a constituent of sulfuric and nitric acids. Oxygen is a very active

element and is the most active in the atmosphere. It is impossible for man to survive without this element. All fires would immediately go out if the oxygen were removed.

Oxygen can be prepared from water by electrolysis. Then if a direct current is passed through water, hydrogen is obtained at the cathode and oxygen is produced at the anode. The electroplater, in most cases, has to guard against oxygen being liberated at the anode in electroplating baths as this lowers the current efficiency of his cell. Earlier it was pointed out that oxygen was also prepared by heating the red oxide of mercury. Both of these are ways in which to obtain this element. If oxygen is desired in the laboratory, it can be prepared by these two methods, but an easier method consists of heating potassium chlorate, a white crystalline material composed of one part potassium, one part chlorine, and three parts oxygen. On heating this material, it will melt around 350°C. Now, if the temperature is increased, soon bubbles of oxygen are released. When oxygen leaves the above compound, a substance is formed consisting of one part potassium and one part chlorine and called potassium chloride. This can be represented in the following way:

$$\text{Potassium Chlorate} = \text{Potassium Chloride} + \text{Oxygen}$$

At this point, we shall digress for a moment. If a test tube is partially filled with some crystals of potassium chlorate and then mixed with some finely powdered manganese dioxide, which consists of one part manganese and two parts oxygen, and the two heated, taking care not to let the temperature go as high as before, it will be found that the oxygen is released much faster than when heating potassium chlorate alone. If the materials which are left behind are analyzed, it will be found that potassium chloride and manganese dioxide are present, i.e.,

the manganese dioxide goes through the reaction unchanged. This is rather an important phenomenon which occurs many times in chemistry. This foreign compound or substance which was added hastened the reaction quite markedly, but, in itself, was not changed one bit. This type of compound is called a catalyst or catalytic agent. A catalyst may be defined as being a material which aids a chemical reaction without itself being permanently altered. Time and again it will be seen how a catalyst aids many chemical reactions to take place faster than they would otherwise. There are many catalysts which are in industrial use today. A good example of this is the use of nickel and platinum in the hydrogenation of oils, or, for the electrochemist or electroplater, the sulfate ion in a chromium-plating bath. If a small amount of sulfate is present chromium will be deposited. If the amount is too large or if this radical is absent, no chromium whatsoever is deposited.

As it was explained before, oxygen can be made very readily in the laboratory by using potassium chlorate, with manganese dioxide as a catalytic agent. Now, if these materials are mixed in the ratio of four parts potassium chloride to one part manganese dioxide and placed in a container provided with delivery tube as in figure II, and the mixture is heated, oxygen will be liberated which can be collected in wide-mouthed bottles which have been previously filled with water. The reason for collecting this gas over water is that oxygen is very insoluble in water. After this the bottles are full of a gas which is assumed to be oxygen. It has been pointed out earlier that if a glowing splint is introduced into oxygen it will burst into flame. If a glowing splint is introduced into one of the bottles containing this gas, the splint immediately begins to burn with a brilliant flame. This is a test for oxygen. There is only one other gas which will act in a similar way, this gas being nitrous oxide. If a piece of ignited charcoal is held in the oxygen the charcoal imme-

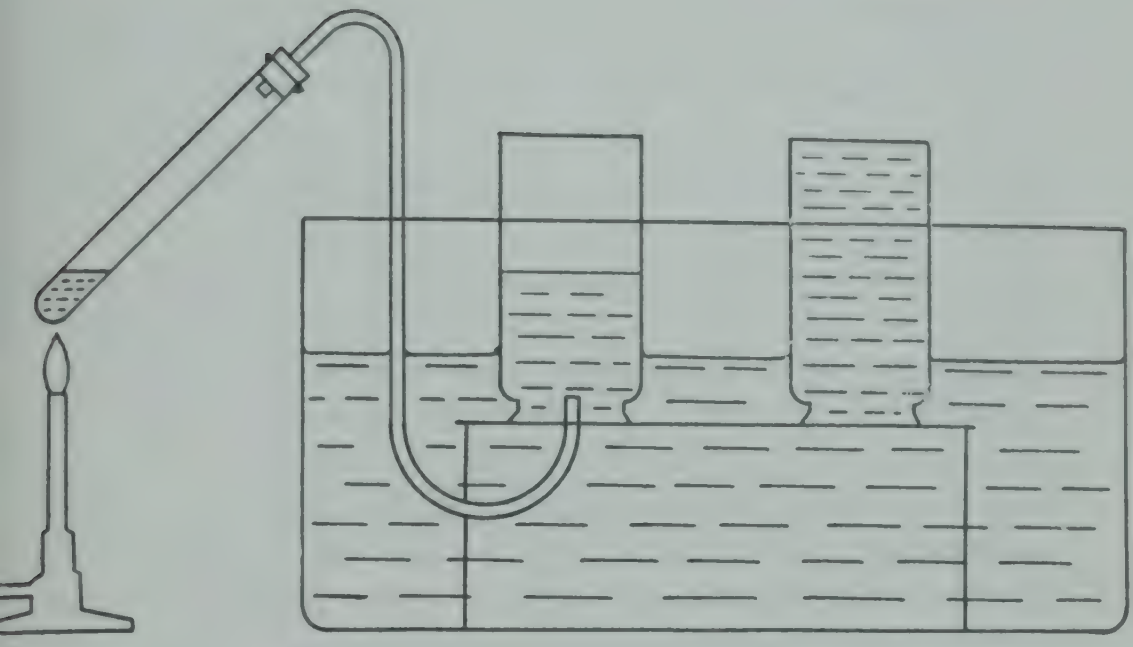

FIG. II

diately begins to burn with a brilliant flame. This is also a test for oxygen. Similarly, if a quantity of sulfur is placed in an iron spoon, ignited, and introduced into another bottle of the oxygen, it also bursts into a characteristic blue flame. It is even possible to burn iron in this gas. If a piece of watch spring is used as a source of the iron and one end is coated with sulfur and ignited, then suspended in a bottle of oxygen, the sulfur burns and, in turn, sets the iron on fire. If a small amount of phosphorus is placed in an iron spoon, ignited, and placed into a bottle of oxygen, a very brilliant flame results. The products of this chemical reaction can be seen, for when this material burns, a white vapor or gas is left behind which is phosphorus pentoxide. This reaction is represented as shown below:

Phosphorus + Oxygen = Phosphorus Pentoxide

From the above experiments, one can readily see that any material, which will burn in air, will burn much faster in oxygen. This gas is colorless, odorless and tasteless, practically insoluble in water and slightly heavier than air. These characteristics are generally called the physical properties of a substance.

It can be seen that oxygen plays an important part in the burning of materials. It might be well worth our time to examine this process to see just what happens in "burning."

Lavoisier did some very important experiments some 150 years ago on the process of burning. He heated some mercury in a closed vessel and noticed that the air, which was enclosed in the vessel, had decreased one fifth of its original volume. On testing for oxygen, in this air, he received a negative result. He did this by introducing a lighted splint into the closed atmosphere above the mercury and it was extinguished. Evidently the material which caused the burning had been removed from the air. Upon examining the mercury in the retort very closely, he found a red powder which had all the properties of red oxide of mercury. This substance previously had been used by another chemist, Priestley, for preparing oxygen. Lavoisier now reasoned that if the red oxide of mercury had come from the union of mercury with the material which was responsible for combustion in air, he would be able to decompose this red compound and produce oxygen. He placed the red material in an apparatus and heated it. On collecting the gas he found a volume which corresponded to the shrinkage of the enclosed air in the first experiment. He now tested for oxygen and found that the material would cause a lighted splint to burst into flame, thus he proved that one fifth of the air was composed of oxygen. He also found that by mixing the residual gas left in the first experiment with a quantity of oxygen necessary to produce its original volume, a gas was produced which possessed all the

properties of ordinary air. These experiments show that oxygen is the only gas in the atmosphere which is utilized in the process of burning.

One often says that a compound is burned up or destroyed, but upon investigation, it will be found that chemically this is not true, as the products which are formed are heavier than the material which was burned. A simple experiment will demonstrate this. If a candle is arranged on a balance pan, as in figure III, and above it is suspended a tube containing sodium

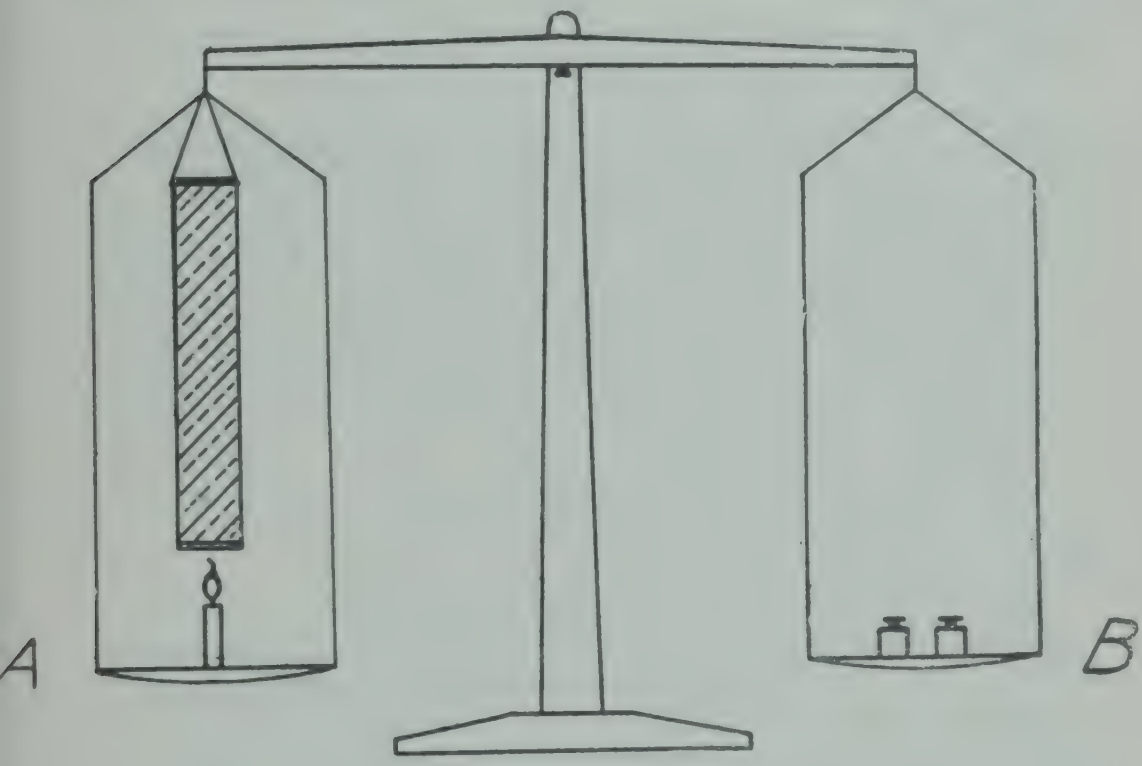

FIG. III

hydroxide (caustic soda), the products of combustion can be weighed. If the scales are carefully balanced by placing suit-

able weights on pan "B" and the candle lighted, it will be noticed that if the candle continues to burn, pan "A" becomes heavier than pan "B," regardless of the fact that the candle rapidly disappears; the reason for this is that when a candle burns it forms invisible gases which are, however, heavy. These gases are water vapor and carbon dioxide. The so called products of combustion are heavier than the original material. The above can also be illustrated by another experiment. If some iron powder is placed in a crucible and carefully balanced on a balance by the aid of weights, it will be found that if heated in a flame until the iron glows, then cooled, and again weighed, the material will have gained quite a bit of weight. If the contents of the crucible are examined, it will be found that the iron is no longer present, but another compound has taken its place which has a red color. This material is iron oxide. These experiments show that when certain substances are heated in the air, the oxygen in the air unites with the materials forming one or more new compounds which are heavier than the original compounds. Using iron as an example, we can say that the iron uniting with the oxygen forms iron oxide. It can be seen that the iron oxide is heavier than iron because it contains oxygen in addition to the iron. An oxide may be defined as being a compound of an element and oxygen.

The union with oxygen is called oxidation. If this reaction takes place very slowly, it does not attract very much attention, for instance, the rusting of iron. If the reaction proceeds very rapidly so that heat and light are produced, more attention is attracted, but in both cases oxides are produced. The latter reactions are generally classified as rapid oxidation or combustion. Thus the burning of coal, wood, oil, gas, and rubber is called a process of combustion.

Spontaneous combustion is a phenomenon which occurs quite

often. If one is so careless as to leave dirty clothes or rags soaked in oil, they will themselves take fire. The reason for this is that the oil is slowly oxidizing and in being oxidized the temperature of the mass is raised to the ignition point, due to the fact that the heat so produced is not conducted away fast enough.

If an electric spark is passed through oxygen, a new material is formed which is called ozone. On investigating, it will be found that this material is much more active than oxygen. This change can be expressed by the equation:

$$\text{Oxygen} + \text{Energy} = \text{Ozone}$$

Different forms of the same element which differ in their energy content are called allotropic forms. Ozone is heavier than oxygen and is more soluble in water. It is a very good oxidizing agent, even better than oxygen, as one would expect. It is used to oxidize different organic compounds and is being used in several French cities to purify the water supply.

QUESTIONS

1. How many elements are there in our universe?
2. Give four chemical changes which take place every day in any electroplating plant.
3. In what ways is chemistry a great aid to the electroplater?
4. Classify the following as elements, compounds or mixtures: Nickel sulfate; cadmium; salt; sodium cyanide; brass; aluminum; concrete; wood.
5. Give the definition of element, mixture and compound.
6. Give the law of definite composition.
7. How could you prove that cupric oxide contains oxygen?
8. Define catalyst.

9. If a metal tarnishes or rusts, does it change in weight?
10. Name four metals that the electroplater deposits which do not rust.
11. Is oxygen formed at the anode or cathode in an electroplating bath?

CHAPTER II

Hydrogen; Diffusion; Three States of Matter

In the preceding chapter, a very important element, oxygen, one that is an ingredient of our water, was discussed. Here, a study shall be made of the other component of water, namely, hydrogen. This element, under natural conditions, is a gas which is colorless, odorless, and tasteless. It does not support combustion, but it burns. It was found that oxygen occurred free in the atmosphere. Hydrogen does not occur in this manner. Illuminating gas contains about 38% hydrogen, and this element is found in combination in many organic and inorganic compounds.

As has been stated, hydrogen combines with oxygen to form the well known compound, water. If this is true, one should be able to decompose, or tear down, this compound and obtain from it hydrogen or oxygen. Thus, if a direct electric current is passed through water containing some acid, one finds that hydrogen is released at the cathode, while oxygen is liberated at the anode. In the electroplating plant, hydrogen is released in large quantities at the cathode in the plating of chromium. All electroplaters are familiar with the bubbling of gas which takes place during electrolysis. This gas, as stated, is hydrogen. If one will observe the anode in a plating plant, it is quite easy to see that a gas is being liberated there. This gas is oxygen, the element which has already been discussed. In the plating

of nickel from nickel sulfate solutions, a small amount of hydrogen is liberated at the cathode. The electroplater has to be very careful of this for if allowed to be liberated in large quantities, the deposit becomes brittle and curls.

Hydrogen can be obtained from water by using very active metals such as sodium or potassium. If a piece of sodium is cleaned and put into water, immediately hissing and bubbling starts. Hydrogen is being liberated from the water in this case according to the equation below:

$$\text{Water} + \text{Sodium} = \text{Hydrogen} + \text{Sodium Hydroxide}$$

Many times the reaction will become so violent that the heat generated will set the liberated hydrogen on fire, and it will burn with a characteristic bluish flame. If the material which is formed is examined, it will be found that the metal has displaced one half of the hydrogen from the water. It combines with the other half of the hydrogen plus the oxygen to form a compound called sodium hydroxide, which is a material composed of sodium, hydrogen, and oxygen. If one touches the water where the reaction has taken place with the fingers and rubs the fingers together, it will be noticed that the solution produces a slick feeling. This is characteristic of the compounds which one calls hydroxides.

If one desires to prepare hydrogen in the laboratory, it is not necessary to use this violent method. The best one to use is the action of the acids on certain metals. Acids are compounds which always contain hydrogen. A study shall be made of these interesting compounds later on. The electroplater is quite familiar with many acids, for instance, sulfuric, hydrochloric, nitric, acetic acids, and many others. If we dilute some hydrochloric acid, which is also known as muriatic acid, with water and then pour the solution over metallic zinc, a rather vigorous

reaction results. If this is carried out in the apparatus as shown in figure IV, the hydrogen can be collected in bottles. The reaction which takes place may be represented as follows:

$$\underset{\text{(Hydrogen \& Chlorine)}}{\text{Zinc} + \text{Hydrochloric Acid}} = \text{Hydrogen} + \underset{\text{(Zinc \& Chlorine)}}{\text{Zinc Chloride}}$$

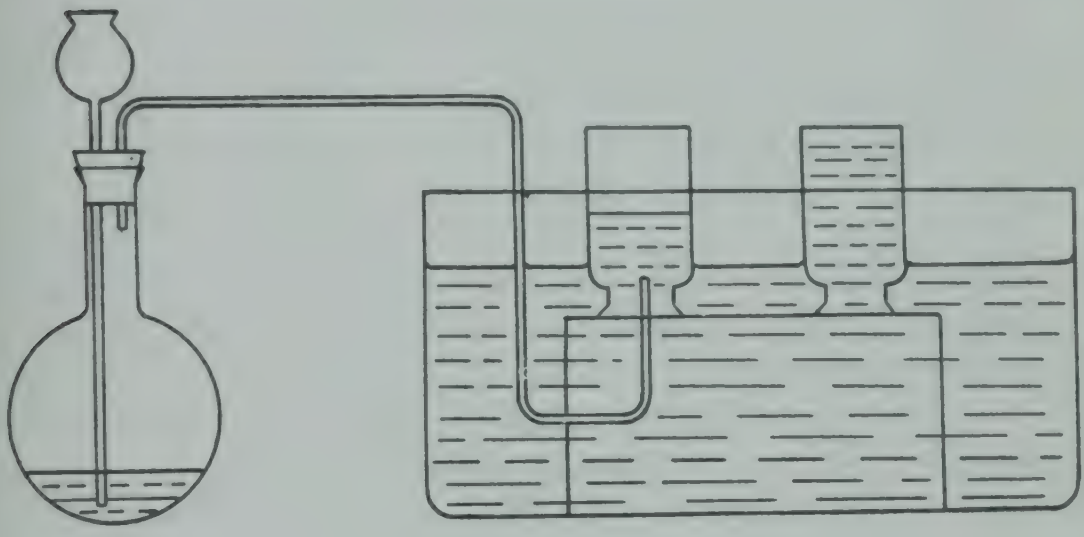

FIG. IV

The product, zinc chloride, obtained by this reaction, is left in the container "A." It is dissolved in the dilute acid, but if this is evaporated the compound may be obtained as a white solid. By observing the equation, it will be seen that the zinc has been substituted for the hydrogen. This type of chemical change is known as displacement. It is possible to use other acids, such as sulfuric acid, acetic acid, instead of hydrochloric acid. At the same time other metals can be substituted for the zinc such as iron, aluminum, magnesium, etc.

Hydrogen is a colorless, odorless, and tasteless gas when pure

It is the lightest of all known substances. In fact it is one sixteenth of the weight of oxygen. For this reason it is used to inflate balloons, etc. It is very slightly soluble in water.

Hydrogen will combine with oxygen to form water. It has been pointed out earlier that oxygen will support combustion but will not burn. It can be proved that hydrogen, although it will burn readily, is not a supporter of combustion. Hydrogen combines with many elements and compounds, thus it unites with chlorine to form hydrogen chloride. It also unites with sulfur to form hydrogen sulfide which is a gas that smells like rotten eggs. Hydrogen has some very peculiar properties. As all electroplaters know, if allowed to be liberated from nickel plating solution, it will cause the nickel to curl away from the cathode, and the resulting plate will be brittle. At ordinary temperatures, it will practically not combine with oxygen, but if heated to 800°C, it will unite with oxygen with great violence. This reaction can be made to take place at ordinary temperatures. Thus, if into a mixture of hydrogen and oxygen some finely divided platinum is introduced, the two elements combine with great violence. If the platinum is examined after the reaction has occurred, it will be found that this material has undergone no change. It merely acts as a catalyst. The platinum in this case played the same part as did the manganese dioxide in the oxidation with potassium chlorate. The catalyst just hastens the reaction without itself being altered.

Hydrogen has an affinity for oxygen, that is, hydrogen tends to combine with oxygen when heated or at ordinary temperature provided a catalyst is present. Hydrogen will combine not only with free but also with chemically bound oxygen, i.e., hydrogen will take the oxygen or unite with the oxygen that is present in black copper oxide. In the apparatus shown in figure V, the tube is charged with copper oxide and heated, then hydrogen passed over the hot copper oxide. Soon the

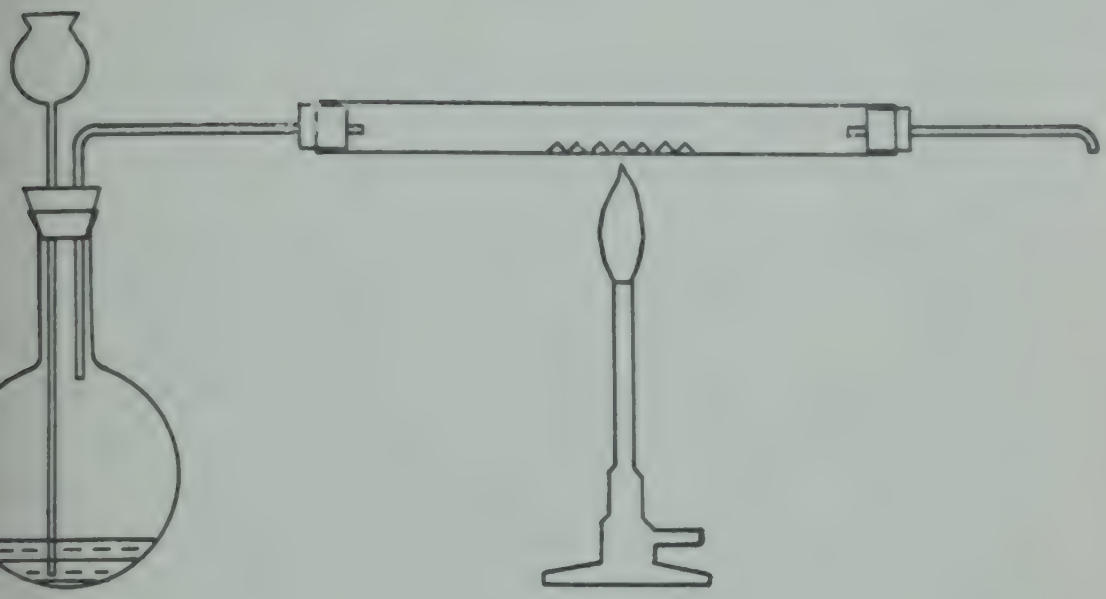

FIG. V

black copper oxide changes over to the characteristic red copper. The oxygen which is in combination with the copper will be set free and unite with the hydrogen, forming water. The same is true if ferric oxide is used instead of copper oxide. This reaction may be expressed as follows:

$$\underset{\text{(Iron \& Oxygen)}}{\text{Ferric Oxide}} + \text{Hydrogen} = \underset{\text{(Hydrogen \& Oxygen)}}{\text{Water}} + \text{Iron}$$

It was stated before that when oxygen combines with materials, oxidation takes place. In the above cases hydrogen has been oxidized. Now, if hydrogen is passed over a material which contains oxygen, we get the inverse of oxidation that is

called "reduction." In chemical sense, reduction is the remova of oxygen from a compound. In the above cases then, th copper oxide was reduced to copper and the iron oxide wa reduced to iron. It can be seen that reduction accompanie oxidation. The noun reduction is derived from the verb "t reduce."

Hydrogen is used to inflate balloons and dirigibles. To balloons, when filled with hydrogen, will rise much faster tha if filled with illuminating gas, because hydrogen is the lightes material known. Hydrogen is used to produce artificial butte and lard from oil. In this case, the hydrogen is made to unit with oils which are thereby converted into solids. This is know as hydrogenation. When hydrogen is burned in oxygen a very hot flame results. This is used to produce very high tempera tures for the melting of platinum, irridium, etc. One of the best uses for hydrogen, at the present time, is the nitroge fixation. In this case the hydrogen is used, in large quantities to combine with nitrogen, forming ammonia.

When two cylinders containing two gases are allowed to be in contact with each other for a few minutes, it will be found upon examination that these gases, regardless of their weights, will be mixed with each other in such a way that equal quantities of both gases will be found in both cylinders. As an example of this, if a cylinder containing hydrogen is placed with its opening uncovered over an open cylinder containing chlorine and allowed to stand for a few minutes, it will be found that both cylinders contain a mixture which is equal in hydrogen and chlorine. This takes place regardless of the fact that chlorine is about thirty-five times as heavy as hydrogen. All gases have this locomotive power. The process by which small parts of gases tend to become uniformly mixed, is called diffusion. The rate at which two gases diffuse into each other is approximately inversely proportional to the square roots of

their densities (see definition of density on p. 26). As an illustration of the above law, it may be said that hydrogen will mix with air four times as rapidly as oxygen. Hydrogen, being the lightest known material, has the greatest speed of diffusion.

In order to explain the properties of gases, a theory has been worked out which is called the kinetic molecular theory. This assumes the following: Gases are made up of exceedingly minute particles called molecules. Molecules of the same substance are all alike. If these molecules are in the gaseous state, they are far apart, but if in the solid state, they are comparatively close together. These little particles are constantly traveling at high speed in all directions. They travel in straight lines except when they hit each other or the walls of the container and bound off. The large empty spaces between the single molecules and their high speed explain why gases diffuse so readily. When the small particles hit against the walls of a container, a force is produced which has a tendency to push out the sides. This force is known as the pressure of a gas. When a certain gas is heated, the small particles move about faster, and in this way exert a higher pressure. Hydrogen and chlorine mix very readily. Hydrogen, being much lighter than chlorine, moves much faster than does chlorine.

About five sevenths of the earth's surface is covered with water. It exists as moisture in many substances. The ground has large quantities of moisture stored in it. Tomatoes contain 95% water, as is true of many other vegetables. The human body comprises about 70% water. This liquid is important to the electrochemist because it is the medium in which electroplating is carried on. For instance, copper sulfate and sulfuric acid are dissolved in water, forming an acid copper sulfate solution which is used for the electrodeposition of copper. The same is true of all other plating baths. Every

one of them contains water as the liquid or solvent. For this reason, it is very important that the electroplater becomes familiar with this interesting compound. Water freezes or turns to solid at 0°C (32°F) and boils or turns to vapor at 100°C (212°F). It is an odorless liquid and, in small quantities, colorless, but large amounts of water show a blue coloration. Water is different from most materials in that when it is cooled from 100°C it gradually decreases in volume until 4°C is reached. At this point, water of a given weight reaches its smallest volume. At 4°C one cubic centimeter of water weighs one gram. Thus, it is possible by this mass per unit volume to define the density of various substances. Water is taken as the standard and its density is one. That is to say, one cc of water, at 4°C, weighs one gram. This may be expressed as follows:

$$\text{Density equals Mass per Unit Volume}$$

$$\text{Density of Water equals } \frac{1 \text{ gram}}{1 \text{ cc}} \text{ equals } 1$$

In the electroplating shop, many liquid reagents are specified not by their density but by their specific gravity. The specific gravity of a material is the relation of its density compared to the density of water. Thus the specific gravity of sulfuric acid is 1.86. This means that a given quantity of sulfuric acid is 1.86 times as heavy as water. This may be stated as follows:

$$\text{Specific gravity} = \frac{\text{Weight of material}}{\text{Weight of equal volume of water}}$$

$$\text{Specific gravity of } H_2SO_4 = \frac{1.86}{1} = 1.86$$

All of us are familiar with the fact that if the temperature drops below 0°C, water turns into ice, and if water is heated to 100°C, steam is formed. The chemist calls this a change of state. Therefore, water has three states, namely, solid, liquid, and gaseous. When water turns into steam or ice, no chemical change takes place, only a physical change results. Water is passing to the gaseous state, even if the temperature is below 100°C. This process is known as evaporation. The electroplater is quite familiar with the fact that the articles which have been plated and rinsed in water soon dry if hung in the air. This is due to the fact that the little particles of water evaporate into the air, leaving the surface behind dry. It is also common knowledge that the water in a plating tank evaporates. Many times nickel sulfate will crystallize on the sides of a tank when the water evaporates and goes to a lower level. The higher the temperature, the faster the evaporation. When the evaporation becomes very rapid, and vapor or gas bubbles through the liquid or solution, it is said to boil. The boiling point of a liquid depends upon atmospheric pressure. The lower the pressure, the lower the boiling point. In order to determine the boiling point of a liquid, the pressure must be taken into account. Thus, water boils at 100°C temperature and 760 mm pressure. The temperature at which a material melts is called the melting point, and a temperature at which a material boils is called the boiling point.

Water will dissolve many materials, for instance, nickel sulfate, sodium cyanide, boric acid, ammonium chloride, etc. The process of dissolving can be considered as a mechanical one. Water is used to dissolve many materials because it is cheap and when some materials (not all) are dissolved in it, the solution formed conducts an electric current. For these two reasons, the electroplater always uses water for dissolving various salts. The liquid which is used in preparing a solution

is called a solvent. The resulting mixture, obtained, e.g., when water has dissolved a salt, is called a solution. An aqueous solution is a solution in which the solvent is water.

When water is electrolyzed, it is broken down into its constituents. If it is possible to build up water from its constituents a further check can be obtained on the composition of this material. It will always be found that two volumes of hydrogen are required to unite with one volume of oxygen to form water. This type of experimentation is known as "synthesis," which means "putting together." If the volume of oxygen required to unite with a given amount of hydrogen is measured, it will be found that two volumes of hydrogen plus one volume of oxygen equals two volumes of steam.

If water is decomposed, regardless of its source, it will always be found to consist of two volumes hydrogen to one volume oxygen. The same is true if hydrogen and oxygen of any derivation are united. They always combine in the same ratio to produce water. If other gaseous reactions are investigated, it will always be found that the volumes of the gases used and produced in a chemical reaction can be represented by the ratio of small whole numbers.

If one desires to determine the relative weights of the elements in a compound, for example, hydrogen and oxygen which combine to make water, the reaction of hydrogen and copper oxide can be used to advantage. Thus, if hydrogen is passed over a weighed amount of copper oxide and the water formed is weighed, the loss in weight of the copper oxide gives the weight of the oxygen used, and the difference between the weight of the water formed and that of the oxygen used is the weight of the hydrogen. If this experiment is performed it will be found that one part by weight of hydrogen combines with 7.94 parts by weight of oxygen to form water. If the amounts of materials present are determined, the experiment is

called a quantitative one. If one does not determine the amounts, but only the identity of the materials present, a qualitative experiment results. In short, one may say that quantitative means how much, while qualitative means what.

There is also another compound of hydrogen and oxygen, called hydrogen peroxide, which differs from water in that two volumes of hydrogen unite with two volumes of oxygen. It was found that one part of hydrogen and 7.94 parts of oxygen by weight unite to produce water. Hydrogen peroxide contains one part by weight of hydrogen to twice 7.94 or 15.88 parts by weight of oxygen.

One of the best ways of manufacturing hydrogen peroxide is to unite cold, dilute sulfuric acid with barium peroxide. This reaction may be expressed as follows:

$$\underset{\text{(Barium \& Oxygen)}}{\text{Barium Peroxide}} + \underset{\text{(Hydrogen, Sulfur \& Oxygen)}}{\text{Sulfuric Acid}} = \underset{\text{(Barium, Sulfur \& Oxygen)}}{\text{Barium Sulfate}} + \underset{\text{(Hydrogen \& Oxygen)}}{\text{Hydrogen Peroxide}}$$

The barium sulfate thus produced is an insoluble, white solid which settles out on the bottom of the container. Hydrogen peroxide is generally sold as 3% solution in water under the name of peroxide or hydrogen peroxide. This solution is used wherever a strong oxidizing agent is needed, e.g., for bleaching cotton, silk, wool and hair, as an antiseptic, cleaning agent, and in nickel plating solutions to depolarize the cathode. Cathode polarization is caused by hydrogen, which is liberated during electrolysis. This film of gaseous hydrogen interferes with the process. Hydrogen peroxide is added to the plating bath, the excess oxygen contained in this compound is liberated and it combines with the hydrogen, forming water. In this way, a troublesome gas is removed, and the plater obtains a smooth deposit of nickel.

QUESTIONS

1. Is hydrogen formed at the anode or cathode in an electroplating bath?
2. Give two examples where large amounts of hydrogen are liberated in electroplating or electrocleaning baths.
3. What is reduction?
4. Name three types of chemical reaction which have been discussed so far.
5. What is diffusion?
6. Give four facts concerning the kinetic molecular theory.
7. Name the three states of matter.
8. What is evaporation?
9. What is the ratio of combining weights of hydrogen to oxygen to form water? To form hydrogen peroxide?
10. Define density and specific gravity.

CHAPTER III

Carbon Dioxide; Carbon Monoxide; Elements of the Atmosphere; Theory of the Atom and Molecule; Symbols of the Elements; Valence; Chemical Equations

In the two preceding chapters two elements and several compounds have been studied. In this chapter, two oxides of carbon, namely, carbon dioxide and carbon monoxide will be discussed. Also, the elements found in the atmosphere will be studied. In the latter part of this chapter the theory of atoms and molecules is given, and finally, symbols of the elements are listed, and methods are proposed for writing chemical equations, using the valences of the elements. The last part of this chapter is very important as the subjects treated there are the basis for chemical calculations.

Carbon dioxide is always present in the atmosphere varying from 0.04 to 1%. Wherever there is combustion, carbon dioxide is produced. For instance, when illuminating gas, wood, coal, fuel oil, gasoline, or any material containing carbon is burned, carbon dioxide is formed. Animals also produce large quantities of carbon dioxide by the slow combustion of food. In the human body, for instance, oxygen is breathed in and carbon dioxide and water vapor are exhaled. The carbon dioxide comes from the oxidation of the foods which contain carbon. If this gas is passed through clear lime water, it unites with the lime and produces a milky solution which contains a pre-

cipitate of calcium carbonate. Therefore, the production of milkiness in lime water, when carbon dioxide is passed through, is a test for the substance.

One would think that the air would become more and more saturated with carbon dioxide due to the many fires which occur, converting carbon into carbon dioxide, and also the large amounts of this gas exhaled by animals. This, however, is not the case, for if the carbon dioxide in the city atmosphere is analyzed, it will be found that the quantity is not higher than that obtained from a sample of air from the country. The reason for this is that the plants breathe in carbon dioxide and use it for food and breathe out oxygen, which is the reverse of the process taking place in animals. This can easily be proved if a green leaf is submerged in water and then placed in the sunlight. Soon it will be noted that bubbles appear on the surface of the leaf and gas is liberated. If this gas is tested it will be found to be pure oxygen.

Carbon dioxide may be prepared by pouring hydrochloric acid over calcium carbonate. It will be noted that gas bubbles appear in the solution and rush to the surface. If these are collected in wide-mouthed bottles, experiments can be performed. Thus, if a lighted candle is introduced into a bottle containing carbon dioxide, the flame is extinguished. Therefore, it is logical to contend that this gas does not support combustion. Furthermore, it will be found that carbon dioxide will not burn. One would expect carbon dioxide not to burn or support combustion as it results from combustion. If a stirring rod is dipped into lime water and withdrawn in such a way that a clean drop remains on the end of the rod and then it is lowered into a bottle of carbon dioxide, it will be noted that the clean drop becomes cloudy or milky. If a beaker is balanced on a scale and then some carbon dioxide poured into it, one will notice that the balance shifts over and the beaker gains

weight. This shows that carbon dioxide is heavier than air. If some litmus paper,* which is impregnated with an organic dye, is introduced into water and then carbon dioxide bubbled through it, the litmus turns red, proving that carbon dioxide, when dissolved in water, is an acid.

When pure carbon dioxide is examined it will be noticed that the gas is colorless, odorless, heavier than air, and slightly soluble in water. The solubility increases with increased pressure and decreases with decreased pressure. The so-called soft drinks on the market today contain large amounts of carbon dioxide dissolved in water. Before opening the cap we note that no gas is visible, but the moment the cap is removed large quantities of the gas effervesce, or bubble off. Carbon dioxide is a gas which will not support combustion or burn as pointed out above. When dissolved in water it forms an acid called carbonic acid. This gas will unite with lime or calcium hydroxide, forming a white precipitate of calcium carbonate. Calcium carbonate is the chemical name for marble.

Carbon dioxide, like water, has three states, namely, solid, liquid, and gaseous. It is very easy to obtain this substance in any of the three forms, thus, by applying pressure, carbon dioxide can be converted to the liquid form. Large tanks of liquid carbon dioxide are sold every day. If we open the valve and allow the liquid carbon dioxide to escape slowly, due to removal of heat by evaporation, the liquid carbon dioxide coming out of the opening freezes to a white snow. In the industry this is called dry ice or solid carbon dioxide.

Carbon dioxide is used in making soft drinks, to extinguish fires, etc. The solid variety is used to produce low temperatures.

When a material containing carbon or carbon itself, burns in an atmosphere containing little oxygen, carbon monoxide is

* The color of litmus paper is purple that turns red when the paper is dipped into an acid and blue when it is dipped into an alkali.

formed. If this gas is analyzed, it will be found that one volume of carbon unites with one half volume of oxygen to give one volume of carbon monoxide. Unlike carbon dioxide, it will burn with a characteristic blue flame, forming carbon dioxide. This gas can be prepared in the laboratory by treating formic acid with concentrated sulfuric acid. Carbon monoxide is a gas which is a little lighter than air and slightly soluble in water. It is colorless and always odorless when pure. The gas is used as a reducing agent.

Carbon monoxide is a deadly poison. This is the gas which makes the exhausts of automobiles so dangerous. One should never start an engine of a car with the garage doors shut. The newspapers report deaths caused by this gas day after day. It is colorless and practically odorless when pure and for this reason one cannot see or smell it, which makes it all the more dangerous.

If carbon dioxide is analyzed, it will be found that the weight of its carbon content compared with that of its oxygen is 1 to 2.66. On the other hand, if we investigate carbon monoxide it will be seen that this ratio is 1 to 1.33. It will be noted that 1.33 is one half of 2.66. Therefore, it can be assumed that for a given amount of carbon, carbon monoxide contains one half of the oxygen contained by carbon dioxide. This is indicated by the names of the oxides, as di means two and mono one.

It has been pointed out that hydrogen and oxygen unite in two different ways. The ratio of hydrogen to oxygen in water is 1.8, and in hydrogen peroxide, 1:16. Carbon and oxygen unite also in two different ways, that is, the weight of the oxygen combined with the carbon in carbon dioxide is twice the amount combined with it in carbon monoxide. The ratio of the weight of oxygen in carbon dioxide to that in carbon monoxide is 2:1. This can be stated as follows: When any two elements, let us say A and B, combine to form more than one

compound, the weights of B which unite with a fixed weight of A are in the ratio of small whole numbers. This is known as the law of multiple proportions.

We have already learned that approximately one fifth of the atmosphere is composed of oxygen. Practically, the rest of the atmosphere is composed of another gas which is called nitrogen. The compounds of nitrogen with other elements are very important in many industries and are absolutely necessary in agriculture.

From the previous discussion it is obvious that if oxygen is taken away from the air, about all that remains is nitrogen. It is true that the remaining compound will not be pure nitrogen, but for our purpose it will be sufficiently pure. The oxygen can be removed in several ways. If a metal is burned in the air, this unites with the oxygen present forming an oxide, and in this way leaves nitrogen behind. Thus, by passing air over copper, iron, aluminum, etc., which has been heated until very hot, the oxygen will be removed as cupric oxide, ferric oxide, or aluminum oxide, and the nitrogen will be left free. Another way to remove the oxygen from the air would be to burn phosphorus in it. Nitrogen is a very lazy element. It does not care to unite with the other elements or compounds and, if forced to unite, it desires to be in the free state again. Therefore, nitrogen compounds are very easily decomposed and are used as explosives.

As has been said above, nitrogen prepared from the air is not pure. It contains other inert gases. This was not known until the year 1894, when it has been found by careful research methods that nitrogen prepared from the atmosphere contains 1% of impurities. Helium, argon, neon, krypton, and xenon are the impurities in nitrogen. One of the best ways to prepare nitrogen in the laboratory is to oxidize ammonia to nitrogen and water by passing it over hot copper oxide. Another

way is to heat ammonium nitrite, which decomposes into nitrogen and water. Due to the difficulty in preserving this compound we generally use in its stead two compounds, sodium nitrite and ammonium chloride, which give the same result. Most of the commercial nitrogen is obtained by converting the air into a liquid. If this liquid is allowed to evaporate, the nitrogen is more volatile than the oxygen and is liberated first. In this way, the two elements can be separated.

Nitrogen is a colorless, odorless, tasteless gas. It is slightly soluble in water. Liquid nitrogen has a boiling point of −195.8°C. As has been stated before, this is a lazy element. It does not support combustion and will not burn. At high temperatures magnesium, aluminum, and a few other elements unite with nitrogen to form nitrides. A very important reaction is the union of this element with hydrogen to form ammonia at high pressures and moderately high temperatures.

Air is composed of nitrogen, oxygen, small amounts of hydrogen, carbon dioxide, water, and the rare gases which were mentioned a few paragraphs back. If the atmosphere is investigated, it will be found that these elements are not combined, but are present only as a mixture. It is possible to separate the different elements by purely physical means. On the other hand, synthetic air can be prepared by putting the elements of air together.

In order to liquefy nitrogen, it is necessary to use very low temperatures and very high pressures. It is impossible to liquefy a gas by no matter how high pressure provided its temperature is above a certain point. This point is known as the critical temperature and varies for different gases.

The most important use of nitrogen is in the production of nitrogen compounds. It can also be used in electric bulbs having a tungsten filament; the nitrogen, being very inert, does not unite with the wire, thus prolonging its life.

Rare gases: argon, neon, krypton, helium, and xenon occur in the air in very small quantities. Cavendish, in 1785, noticed a small amount of residual gas when oxygen and nitrogen had been removed from the air. Lord Rayleigh, in 1895, observed that the nitrogen obtained from the air by the removal of the other known atmospheric substances was heavier than nitrogen obtained by the decomposition of its compounds. Sir William Ramsay found that a residual gas, amounting to 0.93% by volume of the sample of air, resulted after the removal of all gases known at that time. The material thus produced was named argon. The other gases were discovered by much research. These elements are all very inert, even more so than nitrogen. So far it has been impossible to make them unite with other elements.

Helium is the second lightest substance known. It is twice as heavy as hydrogen, but not inflammable, therefore it has largely supplanted hydrogen for inflating balloons and dirigibles. Its buoyant effect is about 90% of that of hydrogen. There are no large sources of helium. It has been found that natural gas in the Texas and Kansas fields contains, in some cases, one to two per cent. In 1930, the richest source of helium yet discovered was reported in southeastern Colorado, containing 7% helium.

So far three very important laws have been studied. To sum these up we may state: (1) Law of conservation of matter: Matter can neither be created nor destroyed. (2) Law of definite composition: Elements always combine in the same definite weight ratio to produce a given compound. (3) The law of multiple proportion: When two elements combine to form more than one compound, the ratio of combining weights of the one compound to those of the other can be represented by small whole numbers.

These laws point toward the fact that there must be some unit particle of matter for each of the elements and compounds.

Common table salt acts like common table salt regardless of where it was mined. Table salt is composed of one part of sodium and one part of chlorine. The salt which is dug out of the mines in New York is identical with the salt that is pumped out of wells in Louisiana or Michigan. There have been many attempts to picture the structure of substances in order to explain their properties. The Greek philosophers worked in this line. Leucippus and Democritus, in the fifth century B.C., put forth a theory of invisible atoms. They had no scientific facts to back their statement; they based it only on the general conception of philosophy. Undoubtedly their work and the work of Newton influenced Dalton, who, in 1807, made public his atomic theory. Dalton did not distinguish between the atoms of an element and the smallest part of a compound. The assumptions of this theory may be stated as follows: Elementary substances are composed of very small parts of matter known as atoms. All atoms of one material have the same properties, but atoms of different materials have different properties. Atoms of different elements combine to form compounds. Since Dalton put forth his famous theory, it has been proved beyond a doubt by the large number of experimental results that agreed with the above statements.

The laws of definite composition and multiple proportion can be explained in terms of Dalton's theory. Considering hydrogen and oxygen, two atoms of hydrogen unite with one atom of oxygen to give two molecules * of water. If water taken from the Atlantic or the Pacific Ocean or from a well is analyzed, it will always be found that the hydrogen and oxygen are in the ratio of 2:1. The combining oxygen will have a definite weight, the combining hydrogen will have a definite weight, and they will always produce the same amount of water provided the

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* The smallest part of a compound is called molecule.

same amounts of hydrogen and oxygen are used. Now to explain the law of multiple proportion. It was shown that one oxygen atom united with two hydrogen atoms to give water. Two oxygen atoms can unite with two hydrogen atoms, producing peroxide, i.e., this compound contains twice as much oxygen as water.

If an element were subdivided until the smallest visible sample of it is left, this would contain a large number of atoms. The atom is a very tiny thing, impossible to see with even the most powerful microscope, therefore, to talk about its weight would be silly. The chemist does not attempt to use the actual weight of each atom, but he uses the relative weights of these atoms. Oxygen is chosen as a standard and its weight is assumed to be 16. The atomic weight of hydrogen is 1. This means that oxygen is sixteen times heavier than hydrogen, or hydrogen is sixteen times lighter than oxygen. Helium, the rare gas which was studied earlier, has an atomic weight of four compared with that of oxygen. Hence, oxygen is four times heavier than, or helium is one fourth as heavy as oxygen. Thus, in the case of water, two atomic weights of hydrogen combine with one atomic weight of oxygen, or they combine in the ratio of 2 hydrogen to 16 oxygen, i.e., in the ratio of one to eight. In the case of hydrogen peroxide there are 2 atomic weights of hydrogen combined with 32 atomic weights of oxygen, which is a ratio of 1 : 16. It can be seen that in hydrogen peroxide there is twice as much hydrogen as in water.

ATOMIC WEIGHTS OF ELEMENTS

	Symbol	*Atomic Weight*
Aluminum	Al	26.97
Antimony	Sb	121.76
Argon	A	39.944
Arsenic	As	74.91
Barium	Ba	137.36

	Symbol	*Atomic Weight*
Beryllium	Be	9.02
Bismuth	Bi	209.00
Boron	B	10.82
Bromine	Br	79.916
Cadmium	Cd	112.41
Calcium	Ca	40.08
Carbon	C	12.010
Cerium	Ce	140.13
Cesium	Cs	132.91
Chlorine	Cl	35.457
Chromium	Cr	52.01
Cobalt	Co	58.94
Copper	Cu	63.57
Fluorine	F	19.00
Gold	Au	197.2
Helium	He	4.003
Hydrogen	H	1.008
Iodine	I	126.932
Iridium	Ir	193.1
Iron	Fe	55.85
Krypton	Kr	83.7
Lead	Pb	207.21
Lithium	Li	6.940
Magnesium	Mg	24.32
Manganese	Mn	54.93
Mercury	Hg	200.61
Molybdenum	Mo	95.95
Neon	Ne	20.183
Nickel	Ni	58.69
Nitrogen	N	14.008
Osmium	Os	190.2
Oxygen	O	16.000
Palladium	Pd	106.7
Phosphorus	P	30.98
Platinum	Pt	195.23
Potassium	K	39.096
Radium	Ra	226.05

	Symbol	*Atomic Weight*
Rhodium	Rh	102.91
Rubidium	Rb	85.48
Selenium	Se	78.96
Silicon	Si	28.06
Silver	Ag	107.880
Sodium	Na	22.997
Strontium	Sr	87.63
Sulfur	S	32.06
Tin	Sn	118.70
Titanium	Ti	47.90
Tungsten	W	183.92
Urenium	U	238.07
Vanadium	V	50.95
Xenon	Xe	131.3
Zinc	Zn	65.38
Zirconium	Zr	91.22

Gases are composed of minute particles called molecules. In the common gases, such as oxygen, hydrogen, nitrogen, chlorine, etc., a molecule is made up of two atoms which are held together by chemical forces. In steam, which is the gaseous form of water, two hydrogen atoms are united with one oxygen atom. It can be seen that the molecules of an element are composed of two or more atoms of the same element, whereas the molecules of a compound are composed of two or more atoms of different elements. In a few cases the molecule of an element consist of one atom. These are said to be monoatomic molecules. Helium and mercury are examples of these.

If a block of ice is heated until it melts into water and the heating continued, water will finally be transformed into steam. The molecules going through these different phases have not been altered chemically but their physical characteristics have changed. If, on the other hand, one tears down the water

molecule into hydrogen and oxygen by the passage of a current, then a chemical change takes place.

The chemist has found that in writing reactions, it is much easier to use symbols than words. For this reason, he has adopted certain symbols to stand for chemical elements. Thus, H stands for hydrogen, Cl stands for chlorine, Na for sodium,* No for nickel, Cd for cadmium, etc. In some cases the first letter of the word has been chosen as its symbol, thus we have C for carbon, H for hydrogen, O for oxygen. Of course, this could not be the general rule because the name of more than one element begins with the same letter. For this reason, cadmium is not designated by C because this represents carbon, but its symbol is Cd. Cu stands for copper for the same reason. N stands for nitrogen, therefore, nickel had to have some other symbol and Ni was chosen. A similar explanation can be given about every symbol contained in the list of elements. At this point, the student should become familiar with the symbols and atomic weights of the more common elements, a list of which is given on page 39. The symbols of elements, besides being abbreviations of their names, also mean definite quantities of the elements. Thus Na stands for one atom of sodium and H stands for one atom of hydrogen, etc. It has already been pointed out that each atom has a definite weight, therefore, H means 1.008 parts by weight of hydrogen, O means 16 parts by weight of oxygen, etc. In most cases, oxygen exists in the molecular form, two atoms of oxygen uniting to give one molecule of oxygen. Therefore, the symbol for a molecule of oxygen is O_2. This symbol not only tells us that there are two atoms to one molecule of oxygen, but it also tells that there are 32 parts by weight (2×16) in one molecule of oxygen.

---

* The Latin name of sodium is natrium.

A molecule may also consist of different elements, thus H_2O is the symbol for a molecule of water. This shows that one molecule of water is composed of one part of oxygen and two parts of hydrogen. It also shows that it is composed of $1.008 \times 2 = 2.016$ parts by weight of hydrogen and $1 \times 16 = 16$ parts by weight of oxygen. Adding these we have 2.016 plus 16 = 18.016, which is the molecular weight of water. Let us consider now another common compound, sulfuric acid. The chemical formula of sulfuric acid is H_2SO_4, i.e., it is composed of hydrogen, sulfur, and oxygen. This formula tells that the molecular weight of this compound is:

$$\left.\begin{array}{lll} H = (1.008 \times 2) & = & 2.016 \\ S = (32 \times 1) & = & 32 \\ O = (16 \times 4) & = & 64 \end{array}\right\} + \qquad \underline{\qquad\qquad} \qquad 98.016$$

A radical is a group of atoms of various elements, which acts as one element in chemical reactions. It is possible, however, to break them up into their constituents if necessary. For example, SO_4 is a radical which is quite stable and is known as the sulfate radical. CO_3 is known as the carbonate radical. OH is known as the hydroxyl radical.

It was found that elements combine with one another in certain definite quantities. This was stated under the laws of definite composition. It is found that different elements have different combining capacities, called valences. The chemist takes as his standard hydrogen which he assumes to be monovalent,* that is to say, having only one arm or hook for binding other elements. The following four formulas illustrate this.

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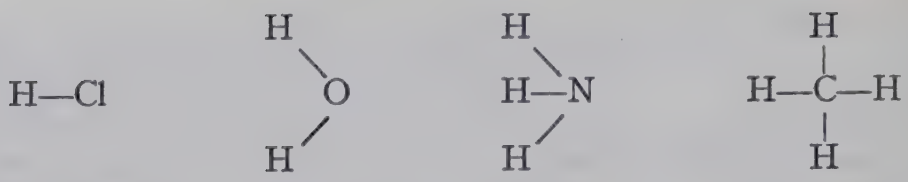
* Monovalent means: having one valence; divalent means: having two valences, etc.



It is seen that one hydrogen combines with one chlorine to form hydrogen chloride. Now if it is assumed that hydrogen is monovalent, then it must also be assumed that chlorine is monovalent, or that chlorine has one hook or arm with which to combine with other elements. The second compound, it will be noticed, has two hydrogens, which combine with one oxygen to form water. If hydrogen is assumed to be monovalent we must assume that oxygen is divalent, that is, oxygen has two hooks with which to take on two monovalent atoms. In the same manner, it will be observed that nitrogen holds three hydrogen atoms, i.e., it has a valence of 3, while carbon holds four hydrogen atoms, i.e., it has a valence of 4. The valence of an element may be measured by the number of hydrogen or chlorine atoms that an atom of the element will hold or displace in a reaction. For instance, a magnesium atom combines with two atoms of chlorine, therefore, the valence of magnesium is two. One sulfur atom combines with two hydrogen atoms to form hydrogen sulfide, therefore, its valence is also two.

Radicals, or groups of elements which react as one unit also exhibit a definite valence. Thus, the sulfate radical, consisting of one sulfur and four oxygens, exhibits a valence of two, i.e., it units with two hydrogen atoms, producing sulfuric acid or hydrogen sulfate. Other radicals also exhibit a definite valence. For instance, the nitrate group ($+ NO_3$), the chlorate group ($- ClO_3$) and the permanganate group ($- MnO_4$) have one valence, whereas the phosphate radical ($\equiv PO_4$) has a valence of three.

COMMON VALENCES

Monovalent		*Divalent*		*Trivalent*	
Sodium	Na	Barium	Ba	Aluminum	Al
Potassium	K	Calcium	Ca	Iron (ferric)	Fe
Ammonium	NH_4	Copper (ic)	Cu	Chromium	Cr
Silver	Ag	Magnesium	Mg	Arsenic	As
Mercurous	Hg	Mercuric	Hg	Antimony	Sb
Chlorine	Cl	Iron (ferrous)	Fe	Nitrogen	N
Bromine	Br	Lead	Pb	Phosphorus	P
Iodine	I	Zinc	Zn	Cobalt (ic)	Co
Fluorine	F	Oxygen	O	Nickel (ic)	Ni
Hydroxide	OH	Sulfur	S	Molybdenum	Mo
Nitrate	NO_3	Carbonate	CO_3	Phosphate	PO_4
Chlorate	ClO_3	Sulfate	SO_4	Arsenate	AsO_4
Bicarbonate	HCO_3	Sulfite	SO_3		

Some of the elements have two or more valences, but most elements have only one. Iron is divalent or trivalent; copper is monovalent or divalent; nitrogen has five different valences in its five oxygen compounds: N_2O, NO, N_2O_3, NO_2 and N_2O_5. However, in most cases, if an element has several valences, one of these is common.

QUESTIONS

1. Give a test for carbon dioxide.
2. Many times a white precipitate occurs when cyanide solutions are exposed to the atmosphere. What has happened?
3. How can you distinguish between carbon dioxide and hydrogen?
4. Why does the concentration of carbon dioxide in the atmosphere not increase?
5. What compounds of nitrogen are important in the plating industry?
6. Give four facts concerning Dalton's theory.
7. Define atom and molecule.
8. What is the difference between a molecule of an element and a molecule of a compound?

9. Define atomic weight.
10. Give the symbols for the following: Hydrogen; oxygen; silver; cadmium; tin; zinc; nickel; lead; gold; copper; aluminum and carbon.
11. Name the elements for which these symbols stand: Sn; Zn; Cd; Ag; Cr; Al; Cu; Ni; Fe; W.
12. Are the following formulas or symbols: Cl; NaOH; I; $-SO_4$; AgCN; Au; C; NaCl?
13. Give the name of the compound and the elements making up the compound of the following: $NiSO_4$; Cd; Cu; $BaCl_2$; NH_4Cl; Al_2O_3.
14. Define valence and radical.
15. Correct if necessary the following: $ZnSO_4$; BaCl; $AgSO_4$; $AlSO_4$; Na_2Cl_2.

CHAPTER IV

Chemical Computations; Chlorine; Hydrogen Chloride and Sodium Chloride

In the preceding chapter several compounds and elements were discussed, and then some theories were explained. In this chapter chemical equations and calculations are put forth. This is a very important study and should be thoroughly understood by those interested. The last part of this chapter deals with muriatic or hydrochloric acid, sodium chloride and chlorine.

A chemical reaction can be expressed by an equation of formulas and symbols. Take, for example, the combination of mercury and sulfur. Here a silver colored liquid is added to a yellow powder and a black substance is obtained. A chemical change has taken place which can be expressed by the following equation:

$$Hg + S = HgS$$

This means that 200.61 parts by weight of mercury unite with 32.06 parts by weight of sulfur to form 232.67 parts by weight of sulfide of mercury. It will be noted that all the starting materials, mercury and sulfur, are on the left, and the resulting material is on the right of the equals mark. (An arrow is sometimes used instead of the equals mark, which means produces or forms.) Therefore, it is essential that the number of atoms

on the left equals the number of atoms on the right. Check over the equation and see if this is true. On the left there is one mercury and one sulfur atom and on the right there is present one mercury and one sulfur atom. Thus, this is a true equation, which is mathematically correct. Take another case, for example, the combination of hydrogen and oxygen to form water.

$$H_2 + O_2 = H_2O$$

It will be noted that two atoms of hydrogen and two atoms of oxygen are on the left, while on the right there are two atoms of hydrogen, but only one atom of oxygen. Therefore, this equation is not right as it stands. It is not a true equation because the left side does not equal the right side. To make the equation true, something must be done in order that the number of atoms on the left equals the number of atoms on the right. As was learned earlier, matter can neither be created nor destroyed. As the equation now stands, one oxyen (O) has been destroyed—at least it is unaccounted for. It was explained in the previous chapter that hydrogen is in the form of molecules (H_2) and each hydrogen atom has a valence of one while oxygen is always in the form of O_2, and each oxygen atom has a valence of two. The formula for water has to be H_2O because oxygen has two valences for attaching two hydrogens. How can this situation be adjusted? Upon close examination of the statement $H_2 + O_2 = H_2O$ it will be noted that one oxygen is missing from the right side of the equation. If a 2 is written in front of the H_2O, there will now be two oxygens on the right the same as on the left, but in doing this the amount of hydrogen atoms has been doubled, that is, we have four hydrogens. Now if a 2 is written in front of the H_2 on the left side of the equation it will now be balanced.

$$2H_2 + O_2 = 2H_2O$$

Check this equation and see if the left side really equals the right side. There are four hydrogens on the left, also, four hydrogens on the right, two oxygens on the left and two oxygens on the right. Therefore, the equation is correct and balanced. Another example will help to learn how to write chemical equations. Take the equation Zinc + Hydrochloric Acid = Zinc Chloride + Hydrogen. If this is written as follows:

$$Zn + HCl = ZnCl_2 + H_2$$

It can readily be seen that this equation is not correct. Zinc has a valence of two, therefore, it will require two chlorines. Thus, the formula for zinc chloride is $ZnCl_2$. Hydrogen is always in the form of H_2 if in the free state. We know that the correct formula for hydrochloric acid is HCl. However, the equation is unbalanced. On the right there are two chlorines, while on the left there is only one, and on the right there are two hydrogens whereas on the left there is only one. How can this equation be balanced? By taking two molecules of hydrochloric acid, 2HCl, the desired result is obtained. The correct equation then will read as follows:

$$Zn + 2HCl = ZnCl_2 + H_2$$

In order to check an equation to see if it is correct, write the equation down after balancing and draw a mark through each element or molecule which appears on both sides of the equation. Thus:

$$\cancel{Zn} + \cancel{HCl} + \cancel{HCl} = \cancel{ZnCl_2} + \cancel{H_2}$$

It will be noticed that all elements and molecules are crossed out, indicating that the equation is balanced, that is, the right side equals the left side.

Before writing the equation one must know (1) that chemical change takes place, (2) what elements or compounds are utilized, (3) what elements or compounds are formed, (4) the formulas of all substances used or produced. Remember to use the molecular formulas for the gaseous elements, thus, O_2, H_2, N_2, Cl_2, Br_2, etc.

If a number is placed before a compound as 2 HCl, it means that there are two molecules of hydrogen chloride which may be written as $2 \times HCl$ or $HCl + HCl$, that is, there must be two hydrogens and two chlorines. In two molecules of water, $2H_2O$, there are four hydrogens and two oxygens. It must be remembered that a 2 placed before a compound doubles the amount of every element in that compound.

All reactions may be divided into four general classes.

TYPE 1, Simple Decomposition

The term, "decomposition" indicates that a compound is breaking up into two or more simpler substances. The break-up of water into its two elements, hydrogen and oxygen, is a good example of simple decomposition:

$$2H_2O = 2H_2 + O_2$$

TYPE 2, Direct Combination

This type of reaction, as can be seen from the name, "combination," is the reverse of decomposition. When two or more substances combine chemically to form one substance, direct combination results:

$$2H_2 + O_2 = 2H_2O$$
$$H_2 + Cl_2 = 2HCl$$
$$C + O_2 = CO_2$$

TYPE 3, Replacement

In this type of reaction one element is replaced by another as the word "replacement" indicates:

$$Zn + 2HCl = ZnCl_2 + H_2$$
$$Zn + H_2SO_4 = ZnSO_4 + H_2$$
$$2Al + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2$$

In the above cases zinc and aluminum replaced the hydrogen of hydrochloric and sulfuric acids. This is also called displacement.

TYPE 4, Double Decomposition

When two compounds react to form two other compounds, the reaction is known as double decomposition. The name implies two materials decomposing. A general statement of this would be:

$$AB + CD = AD + BC$$

Two good examples are as follow:

$$AgNO_3 + NaCl = AgCl \downarrow + NaNO_3$$
$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$$

Incidentally, the first equation expresses the method for determining the chloride in nickel-plating solutions. An arrow pointing down indicates the formation of a precipitate.

Many times the electroplater desires to know how much nickel a given amount of nickel sulfate contains or how much barium chloride should be added to precipitate an excess of sulfuric acid in a chromic acid plating bath. These are important and the electroplater must know how to solve such problems if he expects to become efficient in his field.

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Assume that the amount of copper in copper sulfate is desired. The formula for copper sulfate is $CuSO_4$. Now this means that copper sulfate is composed of one atom of copper, one atom of sulfur, and four atoms of oxygen. Copper has an atomic weight of 63.6, sulfur of 32, and oxygen of 16. Write down these in order.

$$\begin{aligned} \text{Cu} &= 63.6 \times 1 = 63.6 \\ \text{S} &= 32 \times 1 = 32 \\ \text{O} &= 16 \times 4 = 64 \\ & \qquad\qquad 159.6 \end{aligned}$$

Now, on adding up these figures, 159.6 is obtained, which is the total weight of all the elements making up copper sulfate, that is, the molecular weight of this compound. In order to obtain the percentage of copper, the amount of copper which is present in the formula is multiplied by 100 and divided by the weight of the copper sulfate. This may be expressed as follows:

$$\frac{\text{Wt. of copper in } CuSO_4 \times 100}{\text{Wt. of } CuSO_4} = \%\ \text{Cu in } CuSO_4$$

$$\frac{63.6 \times 100}{159.6} = 39.9\%$$

Consequently, there is 39.9% of copper in copper sulfate.

For the percentage of sulfur in $CuSO_4$, the atomic weight of sulfur, 32, is multiplied by 100 and divided by 159.6.

$$\frac{32 \times 100}{159.6} = 20.0\%$$

To calculate the percentage of oxygen:

$$\frac{64 \times 100}{159.6} = 40.1\%$$

This means that copper sulfate is made up of

$$\begin{aligned} \text{Cu} &= 39.9\% \\ \text{S} &= 20.0\% \\ \text{O} &= 40.1\% \\ \hline & 100.0\% \end{aligned}$$

This adds up to give a total of 100% which accounts for all parts of copper sulfate. The percentage composition of a compound can always be calculated from the formula in the same way.

A properly balanced chemical equation gives the following information: (1) What substances react? (2) What substances are formed? (3) The number of atoms or molecules of each substance involved. (4) By using the atomic and molecular weights the amount of the materials involved can be calculated. Take for example the equation:

$$2H_2O = 2H_2 + O_2$$

From the above it is known that (1) water can be decomposed. (2) Hydrogen and oxygen are formed. (3) Two molecules of water are utilized in producing two molecules of hydrogen and one molecule of oxygen. It can further be seen that each molecule of water is composed of one molecule of hydrogen and one atom of oxygen. By writing the molecular weights under the corresponding compound as follows:

$$\begin{array}{lll} 2H_2O = & 2H_2 + & O_2 \\ 2(18) & 2(2) & 32 \\ 36 & 4 & 32 \end{array}$$

It can be seen that 36 parts of water will form four parts of hydrogen and 32 parts of oxygen. If in the laboratory, one decomposes 36 parts of water, in every case, four parts of hydrogen and 32 parts of oxygen will be obtained. The reverse is also true. Thus:

$$2H_2 + O_2 = 2H_2O$$

According to this equation, four grams of hydrogen require 32 grams of oxygen to produce 36 grams of water. This has to be so, otherwise the law of conservation of matter would not be true. Water is always formed with the same ratio of hydrogen and oxygen. It will always be found that four grams of hydrogen unite with 32 grams of oxygen to produce 36 grams of water. The same ratio remains if pounds are used. Thus, four pounds of hydrogen unite with 32 pounds of oxygen to produce 36 pounds of water. As long as the units are the same, namely, grams, pounds, tons, carloads, or shiploads, the results are predictable, but the units must always be the same throughout.

If one desires to know how much water can be formed from 10 grams of hydrogen, using an excess of oxygen the following six steps should be taken:

1. Read problem over carefully.
2. Write the equation.
3. Balance the equation.
4. Write under each atom or molecule the atomic or molecular weight.
5. Multiply the atomic or molecular weight by the number appearing before the symbol in the equation.

6. Write above the symbol any given quantity. In this case the given quantity is 10 grams of hydrogen. Therefore, put 10 grams above the symbol H_2 and x above the material desired which, in this case, is water, H_2O. Thus, writing the equation:

$$H_2 + O_2 = H_2O$$

Balancing:

$$2H_2 + O_2 = 2H_2O$$

Adding atomic or molecular weight:

$$\begin{matrix} 2H_2 + O_2 = 2H_2O \\ 2(2) \quad 32 \quad 2(18) \end{matrix}$$

Multiplying:

$$\begin{matrix} 2(2) + 32 = 2(18) \\ 4 \quad + 32 = 36 \end{matrix}$$

Writing quantity above symbol:

$$\begin{matrix} 10 \qquad\qquad X \\ 2H_2 + O_2 = 2H_2O \\ 4 \quad 32 \quad 36 \end{matrix}$$

The O_2 and its atomic weight 32 do not enter into solving this problem as we assumed that an excess of oxygen is present. Looking closely at what we have, disregarding the equation:

$$\frac{10}{4} = \frac{X}{36}$$

To solve this problem, we need only to cross multiply

$$4X = 36 \times 10$$
$$4X = 360$$

Solving for X

$$X = \frac{360}{4} = 90$$

Thus, 90 grams of water will be produced from 10 grams of hydrogen. Let us check up on the mathematics and see if the answer is correct. By examining the equation it will be seen that for every 4 parts of hydrogen one must have 36 parts of water, that is the weight of water produced from a given weight of hydrogen is nine times as great as that of the hydrogen. This was obtained by dividing 4 into 36. Now, originally there were 10 grams of hydrogen and the weight of water should be 9 times this amount, or 90 grams. In solving an equation of this type, the fixed rules given above should be used. The atomic weights used in all problems can be obtained from the list given in chapter III.

Let us solve another problem. How many grams of barium chloride will be required to precipitate 10 grams of excess sulfuric acid in a chromium plating bath?

1. By reading the problem carefully it will be found that X equals barium chloride and the given quantity is 10 grams of sulfuric acid.

2. $BaCl_2 + H_2SO_4 = BaSO_4 + HCl$

3. $BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl$

4. $\underset{207}{BaCl_2} + \underset{98}{H_2SO_4} = \underset{233}{BaSO_4} + \underset{2(36.5)}{2HCl}$

5. $207 + 98 = 233 + 73$

$$\overset{X}{\underset{207}{BaCl_2}} + \overset{10}{\underset{98}{H_2SO_4}} = \underset{233}{BaSO_4} + \underset{73}{2HCl}$$

$$\frac{X}{207} = \frac{10}{98}$$

$$98X = 2070$$

$$X = \frac{2070}{98} = 21.1$$

That is, 21.1 grams of barium chloride are required to neutralize the 10 grams of excess sulfuric acid.

Now, checking up to see if the answer is correct, it will be noted that for every 98 grams of sulfuric acid in excess one must have 207 grams of barium chloride, or approximately twice as much barium chloride as sulfuric acid. As 10 grams sulfuric acid are present, therefore, there should be approximately 20 grams barium chloride. This is in agreement with the result of our calculation.

Sodium chloride is a salt which is formed by the union of an atom of sodium with one atom of chlorine. Nature has given man a rather abundant and cheap supply of this material, and for this reason, it is used as a starting product for producing other chemicals. If an electric current is passed through a solution of sodium chloride, one might think that the current would decompose the salt into its component parts, sodium and chlorine, but if the products formed are examined, it will be found that instead of sodium and chlorine, chlorine, hydrogen and sodium hydroxide are produced, the latter remaining in solution. This can be explained as follows:

$$2NaCl = 2Na + Cl_2$$

The sodium thus produced is a very active substance, so much so that it will unite with the water at once and form a substance which is called sodium hydroxide, according to the following equation:

$$2Na + 2H_2O = 2NaOH + H_2$$

These two reactions take place simultaneously and in this way chlorine, hydrogen, and sodium hydroxide are produced. Sodium hydroxide and chlorine are very important materials and the industry uses large quantities of them. For this reason large amounts of salt are electrolyzed in order to produce sodium hydroxide and chlorine.

Chlorine can be prepared by several methods in the laboratory, but a very good method is to set free the chlorine contained in hydrochloric acid by allowing manganese dioxide to react with hydrochloric acid according to the equation:

$$4HCl + MnO_2 = MnCl_2 + 2H_2O + Cl_2$$

The chlorine produced by this method is different from the other gaseous elements discussed. Most of the others have been colorless, odorless, tasteless gases, but chlorine is a greenish yellow gas with a very pungent and cutting odor. It is poisonous if breathed in large quantities. This gas is very active, it combines with many metals at room temperature to produce chlorides. Chlorine is used to kill germs. It is soluble in water, forming hydrochloric (HCl) and hypochlorous (HOCl) acids. Chlorine, because of its oxidizing properties is used to a great extent in industry. Chlorine can be produced industrially by the electrolysis of sodium chloride as previously discussed.

If sulfuric acid is gently dropped on sodium chloride it will be noted that a chemical reaction occurs because bubbles of gas

begin to form on the salt and rise. A rather sharp, pungent odor will be noted. This is due to the fact that a gas, hydrogen chloride, is liberated according to the equation:

$$H_2SO_4 + 2NaCl = Na_2SO_4 + 2HCl$$

In this case, it will be noted that hydrogen unites with the chlorine to form HCl and the sodium unites with the sulfate to form Na_2SO_4. This, it will be recalled, is double decomposition. In this experiment, the hydrogen chloride escapes as a gas. If the gas is led into a bottle containing pure water, it will dissolve quite readily, forming hydrochloric or muriatic acid. This acid is very important to the electroplater as it is used for making pickling and etching solutions used in the trade. In the gaseous state HCl is known as hydrogen chloride, but if this gas is dissolved in water it is called hydrochloric acid. It so happens that the gas is very soluble in water. Hydrochloric acid is very active and will react with many elements and compounds. For instance:

$$Fe + 2HCl = FeCl_2 + H_2$$

Here, the iron takes the place of the hydrogen in the acid. This type equation comes under the heading of replacement. Hydrochloric acid is a colorless liquid having a density of about 1.2 grams per cubic centimeter.

When an element unites with chlorine a chloride is produced. Thus, in the above equation, the iron united with hydrochloric acid to form ferrous chloride. In the same manner:

$$Zn + 2HCl = ZnCl_2 + H_2$$

In this case, zinc chloride is formed. All the common chlorides are soluble in water except three. These are silver chloride, lead

chloride, and mercurous chloride. The electroplater desires a test for the chlorides in his nickel plating solutions. It was stated before that all common chlorides are soluble in water except the chlorides of silver, lead, and mercury. Therefore, silver chloride, being insoluble in water, should precipitate out of solution as formed. Chlorides are present in a nickel plating solution in the form of sodium or ammonium chlorides. If a salt of silver is added to this solution, silver chloride should form as a white precipitate which is just what happens. Thus, if a silver nitrate solution is added to a nickel sulfate plating solution, containing ammonium chloride, the white precipitate of silver chloride immediately forms according to the equation:

$$NH_4Cl + AgNO_3 = AgCl + NH_4NO_3$$

The electroplater desires a method for ascertaining the end point. Now after adding a small amount of potassium chromate to the solution, it will be noted that when all the chloride is removed, a second precipitate separates out which is silver chromate. However, the color of silver chromate is reddish-brown and not white. Thus, the color change gives the electroplater an end point or tells when all the chloride has been removed from the solution. The formation of silver chromate proceeds according to the following equation:

$$K_2CrO_4 + 2AgNO_3 = Ag_2CrO_4 + 2KNO_3$$

If hydrogen chloride is decomposed into hydrogen and chlorine by electrolysis, it will be found that an equal volume of hydrogen and an equal volume of chlorine are produced. This shows that hydrogen chloride contains as much hydrogen as it does chlorine, volume by volume. Of course, this is not true of the weights because hydrogen is much lighter than

chlorine. This can easily be proved if the above reaction is reversed and hydrogen chloride is prepared by allowing equal volumes of hydrogen and chlorine to unite. If one volume of hydrogen is placed in a vessel along with one volume of chlorine in the dark and then the mixture is exposed to light, an explosion results. After the reaction takes place, it will be found that there is no free chlorine or hydrogen. This can be represented as follows: One volume of H_2 + one volume of Cl_2 = two volumes of HCl.

QUESTIONS

1. Is a chemical equation a real equation?
2. Write the equation for the reaction of iron and sulfur when heated together.
3. Give the four types of chemical equations.
4. What is the difference between the two forms of HCl?
5. If 24 volumes of chlorine are in a vessel, how many volumes of hydrogen will be utilized in combining with all the chlorine? How many volumes of hydrogen chloride will be formed?
6. An electroplater found that for ascertaining the amount of ammonium chloride present in a nickel plating solution he had used up a solution containing 20 grams of silver nitrate for one liter of the plating solution. How many grams of ammonium chloride were in one liter of plating solution?
7. Calculate the molecular weight and percentage composition of hydrogen chloride.
8. Write the complete balanced equations for the following: Ni + HCl; Pb + HCl.

CHAPTER V

Acids, Bases and Salts; Inverse Proportions; The Gas Laws; Sulfur and Its Compounds; Problems Involving Temperature and Pressure of Gases

In the preceding chapter, the very important subjects of chemical equations and calculations were discussed. These are of extreme value to the electroplater and should be mastered. Chlorine, sodium chloride, and hydrochloric acid were also treated at the end of the chapter.

In this chapter, acids, bases, and salts, as well as the important normal and molar solutions are discussed. Calculations involving inverse proportions are also illustrated, as these are very important to the electroplater. After these subjects have been treated some pages are devoted to molecular weights and their uses. Next follows the discussion of sulfur and some sulfur compounds. One should keep in mind that sulfuric acid and metallic sulfates are used in many plating baths. The methods for making sulfuric acid are given.

Most of the compounds used by the electroplater can be divided into three groups, acids, bases, and salts. A good example of the first group is sulfuric acid which is used in many electroplating plants to clean metals, decrease the pH of a solution, increase the conductivity of plating baths, and neutralize substances which are called bases. Acids have peculiar properties which distinguish them from bases and

salts. All acids contain hydrogen ions.* All acids have a sour taste and turn an indicator, litmus, from blue to red. Examples of acids are hydrochloric, sulfuric, nitric, and acetic acids. Acids unite directly with bases to form water and compounds called salts.

Bases have certain characteristics that can easily be recognized. They turn red litmus blue and, after dissolved in water, produce "slicky" solutions which have a bitter taste. All bases contain the hydroxyl radical, OH. Thus the OH ion is characteristic of bases, whereas the H ion is characteristic of acids. A good example of a base is sodium hydroxide.

It is essential that the chemist has some methods for standardizing the strength of a solution. It is possible to have strong and weak solutions, but chemistry, being an exact science, usually gives the exact concentration for strong or weak solutions. For analysis work it is necessary that the solutions used are made up to a certain defined strength. Just how can the strength of a solution be defined so as to always get uniform results? The electroplater in many instances makes up a solution by adding so many ounces or pounds of salt to one gallon of water. For instance, if twelve ounces of nickel sulfate are added to one gallon of water, the concentration of the solution will not be exactly twelve ounces per gallon, for the simple reason that the volume of salt is added to one gallon of water, which results in a volume of solution larger than one gallon. To make this clear, take the following example. Suppose a solution is desired containing 200 grams of sodium chloride per liter of solution. Now, if one made this up by weighing out 200 grams sodium chloride and then adding a liter of water to the salt, it would be found that the salt solution is well over a liter. There would be a constant error if the volume of every

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* The difference between an atom and an ion will be explained later.

salt added were constant, but this is not true as the volume of nickel sulfate weighing 200 grams does not necessarily equal the volume of sodium chloride weighing 200 grams. In order to do away with this error the salt must be put in a liter flask and filled up with the solvent, so that the solution will be exactly a liter.

The chemist uses among others, molar and normal solutions. A molar solution contains one gram molecular weight * of materials dissolved in one liter of solution. Please note that this definition does not say in one liter of water, but *one liter of solution.* An example will help to make this clear. The gram molecular weight of hydrochloric acid is 36.5 grams. Now if 36.5 grams of hydrochloric acid are dissolved in water the volume of which is less than a liter, and after dissolving the resulting solution is diluted to one liter, the resulting solution has 36.5 grams of hydrochloric acid dissolved in one liter, or 1000 cc. of solution. Another example: The gram molecular weight of sulfuric acid is 98 grams. Now by dissolving 98 grams in, say, 700 cc of water and then diluting the whole to 1000 cc, or one liter, the resulting solution will be M H_2SO_4. M stands for molar solution. If a 0.1 M solution is desired (which is 0.1 as concentrated as the 1 molar solution), 98 is divided by 10 which gives 9.8, and on dissolving 9.8 grams sulfuric acid in 1000 cc of solution, a 0.1 M solution is produced.

Many solid materials crystallize with definite amounts of water encased in their molecules. For example, ordinary copper sulfate, which is $CuSO_4.5H_2O$, has five molecules of water for every molecule of cupric sulfate. This water of crystallization must be taken into consideration when calculating the amount of material to be added in making a solution of definite strength.

*** Molecular weight in grams.**

The reason for this is obvious, as the water will be weighed along with the salt. In figuring the amount of $CuSO_4.5H_2O$ to be dissolved, the $5H_2O$ must be included in the formula weight. For example, a M solution of cupric sulfate is as follows:

$$CuSO_4 \cdot 5H_2O$$

Cu	$63.57 \times 1 =$	63.57
SO_4	$96.00 \times 1 =$	96.00
$5H_2O$	$5 \times 18 =$	90.00
		249.57

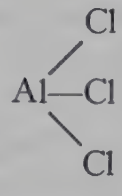
The molecular weight of $CuSO_4$ is 159.57, while that of $CuSO_4 5H_2O$ is 249.57.

For certain types of experiments the chemist uses another type of solution, the normal solution. This contains one gram equivalent weight of material dissolved in one liter of solution. The gram equivalent of a compound is the weight which contains one gram equivalent weight of an element or radical. The equivalent weight or combining weight of an element or radical can be defined as the weight which displaces or otherwise reacts with 8 grams of oxygen or 1.008 grams of hydrogen. The equivalent weight can be calculated by dividing the atomic or formula weight by the valence. The atomic weight of hydrogen is equal to 1.008 and, as this is divided by its valence which is 1, the result is $\frac{1.008}{1}$ which is 1.008. The atomic weight of oxygen is sixteen and its valence is two, and 16 divided by 2 gives 8. Take this reasoning over to a compound. Suppose the equivalent weight of sodium chloride is desired. The molecular weight of sodium chloride is 58.5. The valence of the chloride is 1, therefore, its equivalent weight

is 58.5 divided by 1 = 58.5. The molecular weight of sodium sulfate, Na_2SO_4 = 142. It will be noted that there are two sodiums for one sulfate, i.e., the valence of the sulfate radical is two and it requires two sodiums. Therefore, the equivalent weight of sodium sulfate is 142/2 = 71. Another way of obtaining the amount is to find the hydrogen equivalent. Thus, two hydrogens are required to take the place of the two sodiums, as both have a valence of one. Therefore, the molecular weight of 142 must be divided by 2 to obtain the equivalent weight of sodium sulfate. In this case, 71 grams of sodium sulfate dissolved in 1000 cc solutions gives a 1 N (normal) solution. A 0.1 N solution is obtained by dividing the amount necessary to make a 1 N solution by 10. For sodium sulfate, a 0.1 N solution would contain 7.1 grams of sodium sulfate per liter (1000 cc).

Another example will be used to illustrate the calculation of equivalent weight. Take aluminum chloride. The gram molecular weight of this substance is 133.5 grams, and the gram equivalent weight is $\frac{133.5}{3}$, that is, 44.5. The reason for dividing by 3 is that aluminum equals three hydrogens. The illustration below will help to clarify this:

One Al and three Cl make up $AlCl_3$



Substituting H for Al we have:

H—Cl
H—Cl
H—Cl

Therefore, 1 Al = 3 H, i.e., it has three valences. Thus, one hydrogen is equivalent to one-third aluminum. The table below will serve to summarize all the above.

Compound	*Molecular Wt.*	*N Solution*	*M Solution*
HCl	36.5	36.5	36.5
H_2SO_4	98	49.0	98.0
$AlCl_3$	133.5	44.5	133.5
$CuSO_4 \cdot 5H_2O$	249.57	124.78	249.57

If equivalent quantities of an acid and a base are brought together, they enter into reaction with each other, which is called neutralization. An acid can be neutralized by a base or vice versa. The neutralization can be followed visually, provided certain substances, called "indicators" are added to the solutions. Litmus is a good example of indicators. Purple or red litmus becomes blue when introduced into a basic solution and purple or blue litmus becomes red when placed into an acid solution. Thus, when using litmus one can tell by the color of a solution whether it is an acid or a base solution. It is also possible to find out the amount of an acid or base present in solution of unknown concentration. This is accomplished in case of an acid solution, by adding to the solution of unknown concentration a base solution of known concentration and sufficient to neutralize the acid. When the acid is neutralized, its amount can be mathematically obtained from the amount of base required for neutralization. Let us consider an example. Litmus is added to hydrochloric acid which is contained in a beaker. The solution will assume a red coloration. If some ammonium hydroxide is added in small amounts it will be noted that the red color remains about the same. After some time, however, the color turns into a blue. Thus, the end or neutralization point has been reached.

In the above example, hydrochloric acid was neutralized with ammonium hydroxide, the reaction being:

$$NH_4OH + HCl = NH_4Cl + H_2O$$

Let us assume that the ammonium hydroxide used was of known strength, say 0.1 normal and also that the amount added was 25 cc and that 10 cc of hydrochloric acid was used. To summarize, 25 cc of 0.1 N NH_4OH was used to neutralize 10 cc of HCl of unknown (N) normality. The unknown quantity is the normality of the HCl. In solving this problem an inverse proportion is used. This is different from the direct proportion used heretofore. The reason for this will be seen if the results are analyzed. First, the more concentrated the ammonium hydroxide solution used, the smaller the volume which will be required to neutralize the unknown solution. For instance, a 0.1 N solution of hydrochloric acid contains 3.65 grams of HCl per liter while a N solution contains 36.5 grams of HCl per liter. Therefore, if it takes 10 cc of a 0.1 N solution ammonium hydroxide, it will require only 1 cc of a normal (N) solution. How to express this mathematically? Simply:

$$10 \text{ cc} \times 0.1 = X \times 1$$

Solving for X

$$1.0 = 1X$$

$$X = 1$$

Therefore, X = 1 cc. Let us take this over to the problem and mark down everything that is given:

Given $NH_4OH = 0.1N$

25 cc of the above used to neutralize 10 cc of a HCl of unknown concentration,

Required: Normality of HCl

Think a few minutes and see just what can be found concerning this problem. It will be noted that a larger volume of ammonium hydroxide was required than that of the HCl. From this, it follows that the HCl is stronger than the NH_4OH and the strengths are in the ratio of ten to twenty-five, or the HCl is about two and one half times as strong as the NH_4OH. Setting up the equation one should have:

Normality of base $\times$ cc of base used = normality of acid $\times$ cc of acid used

Substituting the numerical data in the above equation:

$$0.1 \times 25 = X \times 10$$

Solving for X:

$$2.5 = 10X \text{ or } 10X = 2.5$$

$$X = 0.25$$

The normality of the hydrochloric acid is larger than the normality of the base.

Ammonium hydroxide united with hydrochloric acid to form water and another chemical compound. The latter which is called ammonium chloride is a salt and is formed by the combination of an acid and a base. Salt can also be formed by replacing the hydrogen of an acid by a metal. For instance:

$$2HCl + Zn = ZnCl_2 + H_2$$

Here zinc chloride is the salt. Salts are very important to the electroplater as most plating baths contain salts. Thus, a nickel plating solution contains nickel sulfate and ammonium or so-

dium chloride. Tin baths contain sodium stannate or stannite sodium acetate or stannous or stannic chloride. This holds fo most plating solutions.

The Gas Laws

Gay Lussac, in 1805, found that in any chemical reaction the volumes of all gases entering the reaction are to each other as the ratio of small whole numbers. A little later Avogadro explained this by assuming that equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules. For example, one liter of chlorine contains the same number of molecules as one liter of any other gas provided that all gases are at the same temperature and pressure. There will be the same number of molecules in one liter of hydrogen chloride, water vapor, hydrogen, oxygen, or any other gaseous material, e.g., at room temperature and 760 mm pressure. Avogadro made no assumptions as to how many molecules were present in a volume of gas, but it can be clearly seen that comparative weights of the molecules can be obtained by comparing equal volumes of the gases at the same conditions.

Avogadro's theory will help to understand the statement that the molecule of most gases consists of two atoms. If the following reaction is considered,

H_2	+	Cl_2	=	HCl	+	HCl
1 vol. hydrogen		1 vol. chlorine		1 vol. hydrogen chloride		1 vol. hydrogen chloride

it will be noted that one volume of hydrogen unites with one volume of chlorine to produce two volumes of hydrogen chloride. According to Avogadro's theory, two volumes of hydro-

gen chloride contain twice as many molecules as one volume of hydrogen or one volume of chlorine. So it must be assumed that the hydrogen molecules break down into two parts and each part unites with a chlorine atom to produce a molecule of hydrogen chloride. Thus, as the hydrogen molecule contains two atoms of hydrogen, its molecular formula must be H_2 so that its molecular weight will be approximately $2 \times 1 = 2$. If the value of exactly two is given for the molecular weight of hydrogen and one for its atomic weight, this would make the relative weights of the other elements run into fractions, so that the molecular weight of oxygen would be 31.746. Scientists have agreed that the molecular weight of oxygen should be exactly 32 and consequently the atomic weight of hydrogen is 1.008. We can prove with the aid of Avogadro's theory that the molecule of oxygen consists of two atoms.

$$H_2 + H_2 + O_2 = H_2O + H_2O$$

This means that

1 volume hydrogen	+	1 volume hydrogen	+	1 volume oxygen	=	1 volume water	+	1 volume water

It will be noticed in this case that two volumes of hydrogen unite with one volume of oxygen to produce two volumes of water. Therefore, the oxygen molecule broke into two parts to form the water. Thus, the molecular formula of oxygen is O_2.

In the chemical equation the coefficients in front of the symbols of substances in the gaseous form represent the relative volumes of the substances uniting and resulting from the reaction. Take for example the equation:

$$2H_2 + O_2 = 2H_2O$$

This means that two volumes of hydrogen are required to unite with one volume of oxygen, producing, thereby, two volumes of water vapor. If 2000 cc of hydrogen burns to give water, it can be seen at once that one half this volume of oxygen, or 1000 cc are required to unite with this amount.

If a chemist goes to the laboratory and takes a gram molecular weight of hydrogen and then measures the volume of this material at standard conditions, i.e., at 0°C temperature and 760 mm pressure, he will always find that the volume occupied by this gas will equal 22.4 liters. Now if the volume of a gram molecular weight of chlorine (about 71 grams) is taken at standard conditions, it will be found that the volume is equal to the volume of the hydrogen, namely 22.4. In every case the volume of a gram molecular weight of a gaseous substance occupies 22.4 liters at 0°C temperature and 760 mm pressure. It will also be noted that if the gram molecular weight is divided by the density, the result is constant, namely, 22.4 liters.

In 1818, Dulong and Petit observed that if the atomic weight of an element is multiplied by its specific heat the result is a constant of about 6.4. The specific heat of a substance is equal to the number of calories * required to raise the temperature of one gram of material 1 degree Centigrade. It might be pointed out that this law does not hold exactly, but it does serve as a rough guide when one is in doubt about the value of the atomic weight. The atomic weight multiplied by the specific heat is called atomic heat. Taking copper for example: $0.0923 \times 63.6 = 5.88$, while silver gives: $0.056 \times 107.88 = 6.12$.

Sulfur occurs in nature in various parts of the earth. It is found in the natural form in the United States and in combination in Sicily, Iceland, Mexico, and Japan. Iron pyrites, which

* A calorie is the amount of heat required for raising the temperature of 1 gram water 1°C.

is ferrous sulfide, and the sulfides of copper, zinc, and lead are widely distributed. In Louisiana and Texas, a most ingenious process of mining sulfur has been developed. The process consists of boring a hole through a layer of rock, sending hot water down and melting the sulfur, then blowing air under pressure into the hole and forcing out the sulfur. The hole is first bored into the ground and four pipes are introduced. The thickest of these pipes is six to eight inches in diameter. Through the two outer pipes water heated to 180°C is pumped down into the deposit. This temperature is sufficient to melt the sulfur which liquefies at 114.5°C. When the sulfur is in the molten condition hot compressed air is forced down the innermost pipe, and this air drives the sulfur through the remaining pipe to the surface. On reaching the surface, the sulfur is piped to large wooden bins where it is solidified and shipped to various plants.

Sulfur occurs in several crystal forms. Sulfur is in the rhombic form at any temperature below 96°C. It is a yellow solid having a density of 2.06 and melting point of 112.8°C. Monoclinic sulfur is obtained when sulfur is heated above 96°C. Its melting point is 119°C and its density 1.96. The monoclinic slowly changes into the rhombic variety at room temperature. Both of these forms of sulfur are soluble in carbon disulfide, but insoluble in water. As the temperature of sulfur is raised, the color becomes darker and the solution gummier. At 260°C the material becomes so viscous that it will not flow out of a container. The boiling point is 445°C. After boiling, if sulfur is chilled by cold water, a mass remains which is a mixture of the rhombic and amorphous (non-crystalline) sulfur.

Sulfur generally has a valence of two and reacts readily with a great many metals, and other elements, gold and platinum being exceptions. Thus:

$$Fe + S = FeS$$
$$Zn + S = ZnS$$
$$2Ag + S = Ag_2S$$
$$H_2 + S = H_2S$$
$$O_2 + S = SO_2$$

Sulfur is used for the manufacture of sulfuric acid. It is also used as an agricultural germicide to kill different types of insects and germs. Large amounts of sulfur are used in the rubber industry (as a vulcanizing agent), in the making of matches, and in preparation of chemical compounds.

Hydrogen sulfide occurs in volcanic gases, in some oil wells, and natural mineral waters. It has the odor of rotten eggs and can be recognized very quickly by this characteristic smell. It can be prepared in the laboratory by adding hydrochloric acid to ferrous sulfides:

$$FeS + 2HCl = FeCl_2 + H_2S$$

Hydrogen sulfide is a colorless gas, liquefying at −61.6°C. When dissolved in water, it is a weak acid. At room temperature approximately three volumes of gas dissolve in one volume of water. It is poisonous and should not be breathed in large quantities. Hydrogen sulfide oxidizes in the air yielding water and free sulfur. It can also be burned:

$$2H_2S + O_2 = 2H_2O + 2S$$

Free sulfur burns to produce sulfur dioxide as shown below:

$$S + O_2 = SO_2$$

Hydrogen sulfide is very important in qualitative and quantitative analysis as many of the metallic sulfides are insoluble.

$$CuSO_4 + H_2S = CuS \downarrow + H_2SO_4$$

This sulfide is black as are most sulfides. However, zinc sulfide is white, arsenic and cadmium sulfides are yellow and antimony sulfide is orange.

Sulfur dioxide is an oxide of sulfur. One of the best ways of preparing this substance is to burn sulfur in air.

$$S + O_2 = SO_2$$

It can also be prepared in the laboratory by allowing hydrochloric acid to react with sodium sulfite:

$$Na_2SO_3 + 2HCl = 2NaCl + H_2O + SO_2$$

Sulfur dioxide is a colorless gas, having a very disagreeable odor. It can be easily liquefied and is soluble in water. One volume of water dissolves about forty volumes of SO_2 at room temperature. Sulfur dioxide, when dissolved in water, forms H_2SO_3, sulfurous acid.

Another important oxide of sulfur is sulfur trioxide which has the chemical formula SO_3. It is an intermediate product in the manufacture of sulfuric acid, but is usually not isolated.

Sulfuric acid is a very important chemical and many tons are used every year. There are two processes for manufacturing this compound. The first is the contact process which consists of burning the sulfur with oxygen to produce sulfur dioxide and then oxidizing this compound in the presence of a catalyst to sulfur trioxide. This substance is then united with water to give sulfuric acid. Another method of making sulfuric

acid is the lead chamber process which oxidizes the sulfu dioxide to sulfur trioxide by means of nitrogen compound Each of these methods will be discussed below.

In the contact process the sulfur dioxide is obtained by burn ing sulfur with oxygen.

$$S + O_2 = SO_2$$

It is dried, heated to 400°C, passed into a chamber along with oxygen where the two come in contact with a catalyst * which is, e.g., platinum or nickel. This gives the second product, SO_3

$$2SO_2 + O_2 = 2SO_3$$

The sulfur trioxide can be absorbed readily in sulfuric acid which is then diluted to the desired strength. When diluting with water, the following reaction takes place:

$$SO_3 + H_2O = H_2SO_4$$

In the chamber process, nitrogen compounds such as nitrogen dioxide (NO_2) or nitric oxide (NO) acts as the agent for oxidizing SO_2 to SO_3. Thus:

$$2SO_2 + 2NO_2 = 2SO_3 + 2NO$$

The NO produced can now be oxidized by oxygen as follows:

$$2NO + O_2 = 2NO_2$$

The NO_2 thus formed can be utilized again to oxidize SO_2 to SO_3. These reactions take place at room temperature. The

* A catalyst is a substance that promotes or speeds up a reaction, and is recovered unchanged after the reaction is completed.

sulfur dioxide obtained is passed into large lead-lined chambers along with some water vapor, air, and nitrogen compounds. After allowing a time for the gases to mix, the acid formed is dissolved in concentrated sulfuric acid. In order to recover the nitrogen compounds, the gases are washed with concentrated sulfuric acid. All the oxides of nitrogen are dissolved, forming nitrosyl sulfuric acid. With the aid of water vapor, all the oxides of nitrogen are liberated as gases and are collected and utilized again. The reaction may be expressed as follows:

$$2H_2SO_4 + NO + NO_2 = 2H(NO)SO_4 + H_2O$$
$$2H(NO)SO_4 + H_2O = 2H_2SO_4 + NO + NO_2$$

The contact process is simpler than the chamber process, but the catalyst used is very easily poisoned, and when poisoned does not produce sulfuric acid. For this reason, the contact process must have pure starting materials. However, the contact process produces concentrated sulfuric acid. In the chamber process the catalysts are not poisoned and therefore, the starting product can be impure. However, this produces impure sulfuric acid. Moreover the acid produced by the chamber process is diluted and cannot be obtained in the concentrated form. To summarize, the contact process is better for producing pure acid, while the chamber process produces at low cost an impure and dilute product which can be used in many industries without bad effect.

Sulfuric acid is a heavy liquid, having a specific gravity of 1.84. The pure acid is a colorless, oily liquid, and, if heated, will decompose into sulfur trioxide and water. Sulfuric acid dissolves water in all proportions and for this reason is used as a drying agent. It is a dibasic acid, that is, it contains two replaceable hydrogens. These hydrogens can also be displaced one at a time, thus:

$$NaOH + H_2SO_4 = H_2O + NaHSO_4$$
$$NaHSO_4 + NaOH = 2H_2O + Na_2SO_4$$

Hot concentrated sulfuric acid is an oxidizing agent.

$$2H_2SO_4 + C = 2SO_2 + 2H_2O + CO_2$$

If metals that are inactive are dissolved in sulfuric acid, sulfur dioxide is produced. Examples of these metals are copper, mercury, and silver.

$$2H_2SO_4 + Cu = SO_3 + CuSO_4 + 2H_2O$$

On diluting sulfuric acid care must be taken that this process is carried out correctly as large amounts of heat are liberated when the acid unites with water. If precautions are not taken, steam will result, which will spray the hot sulfuric acid in every direction. Therefore, always pour concentrated sulfuric acid very gently and slowly into water, never the reverse.

When in sulfuric acid all the replaceable hydrogen has been replaced by metal, the resulting salts are called sulfates. If one atom of hydrogen is left, the salts are called acid sulfates or bisulfates. Examples of these are (1) sodium sulfate, Na_2SO_4, (2) sodium bisulfate or sodium acid sulfate, $NaHSO_4$. Most of the sulfates are soluble in water, the exceptions being calcium, barium and strontium sulfate. If a test for the sulfate radical is desired, an insoluble compound is produced by adding a soluble calcium, barium or strontium salt to the solution containing the sulfate, and a white precipitate indicates the presence of the sulfate radical. Thus:

$$BaCl_2 + Na_2SO_4 = BaSO_4 + 2NaCl$$

Sulfuric acid is a very important chemical. It is used in the fertilizer industry for the manufacture of ammonium sulfate, for pickling iron and steel, in the treatment of many metals, and for the manufacture of explosives and textiles. In 1930, 7,625,000 tons were produced. Sulfuric acid finds many uses in the metal finishing trade. Whether in pickling or plating bath, sulfuric acid is an important substance for the plater.

An oxide of any non-metal that combines with water to form an acid is called an acid anhydride. Thus:

$$H_2O + SO_2 = H_2SO_3$$
$$H_2O + CO_2 = H_2CO_3$$

Thus SO_2 and CO_2 are acid anhydrides. The oxide of any metal which unites with water to form a base is called a basic anhydride. Thus:

$$MgO + H_2O = Mg(OH)_2$$

Thus MgO is a basic anhydride.

A study of chemistry would be incomplete without discussing gases under different temperatures and pressures. True, the electroplater has very little use for gas laws but one should have a general knowledge of these.

A very important law, concerning the relationship of the volume of gases under different pressures, was discovered by Boyle. He observed that if the pressure of a gas was doubled, the volume was reduced to one half of the original; conversely, if the pressure was reduced to one half, the volume expanded to twice the original, both at constant temperature. This can be stated as a law as follows: The volume of a gas varies inversely with the pressure, that is they are in an inverse ratio. It will be recalled that this type of ratio was studied under

neutralization of acids and bases. It may be said that as t pressure increases, the volume gets smaller. This is only co mon sense. Push down twice as hard on a pump and the pist cuts the volume to one half its original size. This law may stated mathematically as follows:

$$\frac{P_1}{P_2} = \frac{V_2}{V_1} \text{ and } P_1V_1 = P_2V_2 \text{ and } P_1 = \frac{P_2V_2}{V_1} \text{ or } V_1 = \frac{V_2P_2}{P_1}$$

$$\text{or } V_2 = \frac{P_1V_1}{P_2}$$

$$\text{or } P_2 = \frac{P_1V_1}{V_2}$$

Where P_1 = first pressure
P_2 = second pressure
V_1 = first volume
V_2 = second volume

Atmospheric pressure is generally measured in millimeters o mercury, 760 mm of mercury being considered the normal pre sure at sea level. From the above law it follows that if one ha 500 cc of a gas at sea level and then one goes to a mountain to where the pressure was 740 mm, the volume will be larger.

From the equation of V_2, the increased volume can be ca culated.

$$V_2 = \frac{P_1V_1}{P_2}$$

$$V_2 = \frac{760 \times 500}{740} = \frac{380110}{740}$$

$$V_2 = 513 \text{ cc}$$

Thus, there is an increase of 13 cc.

Charles, 1787, observed that any gas when cooled decreased in volume. Quantitatively, if the temperature of a gas was lowered 1° C its volume was decreased by 1/273. From this it follows that at −273° C the volume of any gas would disappear. However, all gases become liquid before reaching −273° C, which is called the absolute zero point. The temperature scale having −273° C as starting point is called absolute temperature or degrees Kelvin, from the name of the eminent English physicist, Lord Kelvin. Degrees Centigrade can be converted into degrees Kelvin by adding 273 to the number of centigrades, e.g., 20° C = 20 + 273 = 293° K. Charles' law is as follows: The volume of any gas varies directly as the absolute temperature. If one doubles the temperature of a gas, the volume also doubles provided the pressume remains constant. This may be stated mathematically as follows:

$$\frac{V_1}{V_2} = \frac{T_1}{T_2} \text{ or } V_1T_2 = V_2T_1 \text{ or } V_1 = \frac{V_2T_1}{T_2} \text{ or } V_2 = \frac{V_1T_2}{T_1}$$

and

$$T_2 = \frac{V_2T_1}{V_1} \text{ or } T_1 = \frac{V_1T_2}{V_2}$$

Where V_1 = first volume
V_2 = second volume
T_1 = first temperature in °K
T_2 = second temperature in °K

An example will make this clear. 200 cc of a gas at 273 degrees K is raised to 473 degrees. What is its volume provided the pressure remains constant? In this case V_2 is desired.

$$\frac{V_2}{T_2} = \frac{V_1}{T_1}, \; V_2 = \frac{V_1T_2}{T_1}$$

$$V_2 = \frac{200 \times 473}{273}$$

$$V_2 = \frac{94600}{273}$$

$$V_2 = 346 \text{ cc}$$

Thus, the volume will increase from 200 cc to 346 cc provided the pressure remains constant.

Charles' law is true also of pressure at constant volume that is, the pressure of gases increases directly as absolute temperature at constant volume.

It is possible to take into consideration the temperature pressure and volume relationship. In other words we can combine Charles' and Boyle's law as show below:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \text{ or } P_1 = \frac{P_2V_2T_1}{V_1T_2} \text{ or } P_2 = \frac{P_1V_1T_2}{T_1V_2}$$

$$V_1 = \frac{P_2V_2T_1}{T_2P_1} \text{ or } V_2 = \frac{V_1T_2P_1}{P_2T_1}$$

$$T_1 = \frac{P_1V_1T_2}{P_2V_2} \text{ or } T_2 = \frac{T_1P_2V_2}{P_1V_1}$$

A problem will help to illustrate this. 200 cc of a gas at 700 mm pressure and 200 degrees K is heated to 300 degrees K and has a volume of 600 cc. What is the final pressure?

$$P_2 = \frac{P_1V_1T_2}{T_1V_2}$$

$$P_1 = 700 \text{ mm}$$

$V_1 = 200$ cc

$T_1 = 200°K$

$V_2 = 600$ cc

$T_2 = 300°K$

$$P_2 = \frac{700 \times 200 \times 300}{200 \times 600} = \frac{42{,}000{,}000}{120{,}000} = 350 \text{ mm}$$

QUESTIONS

1. Give four properties of bases.
2. Give four properties of acids.
3. Give four properties of salts.
4. Write equations for the following reactions: $NaOH + HCl$; $KOH + H_2SO_4$; $NH_4OH + H_3PO_4$.
5. Write the weights which will be required to give one liter of the normal and molar solutions of the following compounds: $AlPO_4$; Na_3PO_4; HCl; K_2SO_4; $CuSO_4 \cdot 5H_2O$; $Cd(Cu)_2$; $NiSO_4 \cdot 7H_2O$.
6. 50 cc of a 0.1 normal HCl solution was required to neutralize 25 cc of an unknown NaOH solution. What is the normality and molarity of the solution?
7. Give Avogadro's theory.
8. In the case of gases, what do the coefficients of the formulas represent?
9. Explain by equation how to test for a sulfide; a sulfite; and a sulfate.
10. How many grams of copper sulfide will be formed if 50 grams of H_2S unite with copper sulfate to form copper sulfide?

CHAPTER VI

True Solutions; Suspensions; Emulsions; Colloidal Solutions and Atomic Weights

In the previous chapter acids, bases, salts, molecul weights, sulfur and sulfur compounds were studied. The i portance of neutralization was stressed and the inverse propo tion was introduced.

In this chapter, true solutions and their properties as well suspensions, emulsions, colloidal solutions, and the determin tion of atomic weights are discussed.

In order to produce a solution, it is necessary to have tw substances which are soluble in each other. Thus sodiu chloride can be dissolved in water to form a solution. In th case, the water is called the solvent and the salt is called t solute. In true solution there is no settling of solute. If sodiu chloride is dissolved in water and placed in a tightly clos vessel from which water cannot evaporate, no sodium chlori will settle to the bottom. It is a perfect mixture, or it may said that the solution is homogeneous. If the sodium chlori solution is passed through a filter, none of the salt will be filter out. When a solid and a liquid are so intimately mixed th particles of the solid cannot be seen, even with a microscope, t mixture is called a solution. It may be pointed out in this co nection that two liquids can form a solution as well as a liqu and a gas. If the mixture has particles which can be se

under the microscope, it is not a true solution but a suspension. If two liquids do not mix intimately, but minute droplets of one liquid are suspended in the other, the mixture is called an emulsion. Milk is a good example of this. Whereas solutions do not settle out, suspensions or emulsions will settle out with time.

A solvent has been defined as the substance which dissolves the solute. Water is a very good example of solvents. Many compounds dissolve in water, forming a solution. Most acids, bases, and salts are soluble in water. Some organic liquids are also good solvents. Thus, carbon tetra chloride is a good solvent for organic compounds such as grease. The electroplater is primarily interested in water as a solvent and the metallic salts, such as the salts of nickel, copper, and zinc, as solutes. Water is a very good solvent for metallic salts. However, in the case of degreasing with trichlorethylene, which is so important, the electroplater makes use of the fact that this organic compound will dissolve oils and greases present on the metallic surfaces.

The amount of solute which is dissolved in the given amount of solvent is known as the concentration of the solution. If there are 100 grams sodium chloride per liter of water, of course, the concentration is 100 grams sodium chloride per liter. When large amounts of solute are dissolved in the solvent, concentrated solutions result. Thus, silver nitrate is very soluble in water and a concentrated solution can be made; 213 grams of silver nitrate will dissolve in 100 grams of water. A dilute solution is one in which a small amount of the solute is present in the solvent. Dilute aqueous solutions can be made concentrated by boiling off part of the water. If the boiling is continued the solution can be evaporated to dryness. In this case all the water is boiled off, leaving behind all the solids as the dry material.

A saturated solution is obtained when the maximum amount

of solute is dissolved in the solvent at a given temperature an the solution remains unchanged if an excess of the solute i added. An example might make this clear. Taking, fo example, silver nitrate, at 18°C, it is possible to dissolve 213. grams of this salt in 100 grams of water. It is possible, b certain means, to dissolve more silver nitrate in water but thi results in an unstable solution known as supersaturated solu tion. However, a supersaturated solution, being unstable, i some crystals of silver nitrate are placed in the bottom of th container, the excess solute will crystallize out of solution an a saturated solution will result. One can see that a saturate solution will hold the maximum amount of solute in the solvent while the solution is in contact with the solute in the crysta form. It is impossible to keep a supersaturated solution whe crystals of the solute are in contact with the liquid.

As a general rule, all solids are more soluble with an increas of temperature, however, there are some exceptions. Potassium nitrate is about seven times more soluble at 70° than at 8° Therefore, in specifying the solubility of salts it is always essen tial that the temperature at which the solution is to be made i specified. It may be stated, as a general rule, that gases are les soluble with an increase in temperature. It should be empha sized, at this point, that different salts have different solubilities As has been stated before, silver nitrate is very soluble. Copp sulfate is also very soluble. At 80°C, about 57 grams of copp sulfate will dissolve in 100 grams of water. Sodium nitrat is even more soluble, at 20°C, approximately 88 grams of thi salt will dissolve in 100 grams of water. However, silver sul fate is only sparingly soluble. Only 0.55 grams dissolve in 10 grams of water at 18°C. Some salts being practically insoluble they can be almost completely precipitated. Barium sulfate i almost insoluble in water. At 18°C only 0.00023 grams of thi salt will dissolve in 100 grams of water. The electroplate

makes use of this in determining the sulfate content of chromium-plating solutions. These solutions contain a soluble sulfate. If a soluble barium salt is added, such as barium chloride, the insoluble barium sulfate is formed. This can be weighed and the amount of sulfate calculated from the results. Thus, the electroplater can quantitatively determine the amounts of different radicals in his plating solutions. It can be seen that a solution can be saturated without being concentrated. For instance, a small amount of barium sulfate present in water forms a saturated solution but it is far from being concentrated.

Earlier the fact was mentioned that by evaporating a solution to dryness the solute is recovered, in the case of solids and liquids, as a dry solid. The dry solid will separate out in the form of crystals. These crystals can also be obtained by preparing a saturated solution at a high temperature and allowing it to cool, to separate some of the crystals. It will be noted that the same solute will always crystallize in the same shape. Thus, ordinary table salt (sodium chloride) crystallizes in the form of cubes. For this reason the crystalline forms of material can be used many times to identify the substances present.

Many solids crystallize with water of crystallization. A good example of water crystallization is shown when copper sulfate crystallizes. It will be found that five molecules of water accompany the copper sulfate, the molecular formula of crystalline copper sulfate being $CuSO_4.5H_2O$. This water of crystallization can be easily separated from the copper sulfate by heating. Such a salt is said to be dehydrated or anhydrous. The salts containing water of crystallization are often called hydrates. Anhydrous copper sulfate, $CuSO_4$, is white, while $CuSO_4.5H_2O$ is blue. If water of crystallization is lost at room temperature, the process is called efflorescence. The opposite may also take place, that is, water may be absorbed from the atmosphere by the salt. This process is called deliquescence.

If a compound is dissolved in a solvent, a definite increa in the boiling point or decrease in the freezing point takes pla This change has been found to be directly connected with t molecular weights of the dissolved substances. The boili point of the solution is elevated 0.52 if one gram molecul weight of a non-volatile, non-ionizing substance is dissolv in 1000 grams of water. The freezing point of the solution lowered 1.86°C for every gram molecular weight of substan dissolved in 1000 grams of water. This helps to determine t molecular weights of many solids and liquids.

Many gases dissolve in water. Thus:

$$H_2O + CO_2 = H_2CO_3 \text{ (carbonic acid)}$$
$$NH_3 + H_2O = NH_4OH \text{ (ammonium hydroxide)}$$

Ammonium hydroxide is very useful to the electroplater. Gase may be divided into three groups according to their solubility

(1) Very soluble: ammonia in water, hydrogen chloride i water, and sulfur trioxide in water
(2) Fairly soluble: carbon dioxide in water, chlorine in wate and hydrogen sulfide in water
(3) Slightly soluble: oxygen, hydrogen, and nitrogen in wate

Henry discovered that an increase in pressure always in creased the quantity of gas going into solution. This is rathe logical because the harder one pushes on a gas the more it wi have a tendency to dissolve in the water.

Solutions seem to be similar to gases in that the molecule of the dissolved materials move around through the molecule of the solvent.

Colloidal chemistry, according to Bancroft, is the chemistr of grains, drops, bubbles, filaments, and films. Grains may b defined as small solid particles, drops as small liquid particles and bubbles as small gas particles. In the case of filaments, a

dimensions except one are small, while in films only one dimension is small. In every case, these particles are completely surrounded by or dispersed in other materials. The diameter of these particles is from 200 millimicrons down to one millimicron, which is one-millionth of a millimeter. Colloidal substances have been mentioned before. Milk, which is an emulsion, consisting of fat dispersed in water was used as an illustration. Suspensions are mixtures which will settle out on standing. Muddy water is an example. Colloidal particles are not as small as the solute particles of true solutions, but they are smaller than particles in a suspension. Thus, one may say the colloidal solutions lie between true solutions and suspensions. It is quite possible for colloidal solutions to appear clear to the eye or under an ordinary microscope. However, if a strong beam of light is passed through a colloidal solution the path of the particles becomes visible at once due to the fact that the particles suspended in the solution have a surface sufficiently large to reflect the light. This phenomenon is rather common and may be seen when one is standing in a dark room and a ray of light penetrates through a crevice; the atmosphere being polluted with dust, this makes the beam of light visible. An apparatus which is called the ultra-microscope is built to make colloidal particles visible. It is possible to estimate the size of particles by simply observing the amount of light which is reflected. If colloidal suspensions are examined under the microscope, it will be found that the suspended particles are continually moving around from place to place. This was observed by Brown in 1837, and is called the Brownian movement. This motion is due to the constant bombardment of the colloidal particle by the molecules of the material in which it is dispersed.

It is rather important to point out that in all colloidal solutions, the substance which is dispersed is insoluble in the dispersing medium. Milk is a colloidal solution of fat in water,

the fat, of course, being insoluble in water. The dispersed substance has very little effect upon the freezing point and boiling point of the solvent. This is due to the fact that generally the concentration of the particles is so slight that the effect is hardly noticeable. Particles of true solutions are capable of migrating through a semi-permeable membrane, while colloidal solutions as a general rule, are too large to do this. Therefore, it is possible to separate a colloidal solution from a true solution, using a semi-permeable membrane, e.g., parchment paper. This procedure is known as dialysis and may be illustrated as follows. Suppose some salt is dissolved in milk. If the mixture is placed in a cup, the opening of which is covered with parchment paper, and the whole lowered into a container of water, the salt will slowly migrate through the parchment paper, leaving behind the milk.

In many cases small colloidal particles combine with each other to produce a larger particle. Soon a point is reached where the particle formed is too large to remain suspended. In this way, the particle precipitates out of solution. Precipitation can be prevented by the presence of certain substances which will prevent the union of colloidal particles. The substance added generally forms a protective film or coating around the small colloidal particles, thus preventing them from uniting with one another. These added substances are generally called protective colloids. Thus, gelatin, a protective colloid, is often added to colloidal solutions to prevent precipitation. Very fine particles of matter suspended in the air also form colloidal solutions. Fog and smoke are good examples. Colloidal particles always carry an electrical charge. This may be proven by the fact that if a colloidal solution is electrolyzed the dispersed particles will generally migrate to the anode or cathode. This shows that the colloid has either a positive or a negative charge. For example, an arsenious sulfide colloidal solution can be electro-

lyzed and it will be found that the yellow sulfide particles move toward the positive pole. Many metals and metallic sulfides bear negative charges when dispersed which means that they will migrate to the positive pole. This is also true if the colloid is suspended in a gas instead of a liquid, that is, the solid or liquid particle will migrate to either the positive or negative pole. Cottrell, an American chemist, applied this phenomenon to the industrial purification of gases. He found that smoke fumes from furnaces, dust from grinding processes, etc., could be eliminated by electrolysis. In some cases an industrial hazard is removed and in other cases, not only the industrial hazard is removed, but also valuable materials are recovered which would otherwise be carried off into the atmosphere. The apparatus for precipitating these colloids consists of a pipe about twelve inches in diameter and ten to thirty feet long. Inside the pipe is suspended a metallic conductor, generally a chain or rod, and both the pipe and the rod are charged electrically, the chain or rod having a charge opposite to that of the pipe. A very high potential is used so that the air is rendered conductive. As the smoke or dust passes through the chamber, the particles being positively or negatively charged migrate either to the negative or positive pole and adhere to the container, while the clean air passes on to the atmosphere. Thus, smoke and dust can be eliminated in the industrial plants. One cubic centimeter of thick smoke may contain five million solid particles.

Colloidal chemistry is becoming very important to the electrochemist or electroplater. In the first place, colloidal solutions are being used more and more for cleaning baths. The solid particles dispersed in solutions produce a rubbing or scouring action on the metal to be cleaned and in this way assist in removing grease or dirt. Also the surface of the colloidal particles may adsorb the oil or grease. Colloidal particles may also be used as addition agents to produce better deposits. Good exam-

ples of solid particles in cleaning solutions are silicates and aluminum compounds, while gelatin, albumen, and licorice are examples of addition agents.

As it has been explained before oxygen is given an arbitrary atomic weight of 16; using this as starting point, every other element will have a corresponding weight, thus, hydrogen will be 1.008, aluminum 27, cadmium 112.41, and magnesium 24.32. If the percentage of each element in a compound is divided by the atomic weight of the element in question, the simplest formula expressing the composition of the material will be obtained. The simplest formula gives only the ratio of the atomic weights of the elements, and does not tell the real formula weight. To illustrate this, let us consider a compound of hydrogen and carbon, both containing 7.75% hydrogen and 92.25% carbon. The simple formula is calculated as follows: 7.75 divided by 1.008 = 7.69 and 92.25 divided by 12 = 7.69, that is the ratio is 1:1, there is one part of hydrogen to one part of carbon which would give the formula of CH. Now the same ratio can be used to represent many chemical compounds. For instance, it may be CH, C_2H_2, C_3H_3, C_4H_4, C_5H_5, and on indefinitely as long as there are as many carbon atoms as hydrogen atoms. Thus, it can be seen that the simple formula gives the ratio of carbon to the hydrogen, but does not tell how many carbons and hydrogens are present in each molecule. In order to know the true formula other information must be obtained. The formula CH represents a compound having a molecular weight of 12 + 1 = 13. On finding the molecular weights of C and H compounds, none has a molecular weight of 13, but one does have a molecular weight of 26 and thus the true formula of this compound is C_2H_2.

It has been pointed out earlier that the atomic weight × the specific heat = atomic heat. This is known as the law of Dulong and Petit. Thus, if the atomic heat, which is generally

a constant and the specific heat are known, one can calculate the approximate atomic weight. The molecular weight of a compound can be obtained as the weight of 22.4 liters in gas form at standard conditions. The molecular weight of a compound can also be determined by the boiling point rise or freezing point lowering method as has been pointed out. It may be assumed that the smallest amount of an element found in a gram molecular weight of its compounds is the atomic weight of that element.

As it has been previously explained normal solutions contain the equivalent weights of substances. The equivalent weight is also called combining weight as it represents the weight of an element which combines with other elements to form compounds. The combining weight of oxygen is 8 grams, and the combining weight of any other element is the number of grams of the element which combine with 8 grams of oxygen. Some elements have more than one combining weight. For example nitrogen has five combining weights, its oxygen compounds being: nitrous oxide (N_2O); nitric oxide (NO); nitrogen trioxide (N_2O_3); nitrogen tetroxide (N_2O_4) and nitrogen pentoxide (N_2O_5). It can be said that the atomic weight of an element is equal to its combining weight or some multiple of it. The combining weight is generally multiplied by a small whole number like one, two, three, or four. The atomic weight of sodium or hydrogen is equal to its combining weight, but the atomic weight of cupric copper is the double of its combining weight. In general, the combining weight multiplied by the valence of an element gives the atomic weight. Thus, for aluminum, the combining weight is 9 and its valence is 3. Therefore, its atomic weight is 27.

During the last few years some very good research work has been done on the elements, which has changed many of our views and has explained many facts. For instance, scientists

sought to explain why the atomic weight of some elements is not a whole number. According to the latest developments the atomic weights found by us are the averages of the atomic weights of different types of atoms of the same element. The different atoms of the same elements are called isotopes. The isotopes have the same chemical properties but slightly different atomic weights. For example, chlorine has two isotopes, whose atomic weights are 35 and 37 respectively. Many elements have these and lately Urey has found that even hydrogen has isotopes.

QUESTIONS

1. Define and give an example of a solution; solvent; solute; dilute solution; concentrated solution; saturated solution and a super-saturated solution.
2. Why does stirring a plating bath make the solids dissolve more rapidly?
3. What is the percentage of water of crystallization in copper sulfate ($CuSO_4 \cdot 5H_2O$)?
4. 10 cc of an 0.2 normal hydrochloric acid solution neutralizes 25 cc of an unknown base. What is the normality of the base?
5. Give two examples of the industrial application of colloidal solutions to electroplating.
6. How would you prove that colloidal particles have definite electrical charges?
7. 20 grams of nickel unite with sulfuric acid solution. How many grams of $NiSO_4$ are formed?
8. What is the difference between the atomic weight and the combining weight?
9. Define isotopes.
10. What is the basis for our molecular weight scale?

CHAPTER VII

The Compounds of Nitrogen; Ions; Electrons and Ionization

THIS chapter deals with the compounds of nitrogen and their properties.

If ammonia gas is passed over hot copper oxide it is decomposed. Water and nitrogen are formed. On the other hand, if ammonia is passed over hot magnesium, hydrogen is set free. Thus, by breaking ammonia down into its components, it is found that it consists of two gases chemically combined with each other, namely hydrogen and nitrogen. The molecular formula of ammonia is NH_3. Ammonia is soluble in water and the aqueous solution is a base called ammonium hydroxide.

$$NH_3 + H_2O = \underset{\substack{\text{ammonium}\\\text{hydroxide}}}{NH_4OH}$$

It is quite possible to decompose ammonium hydroxide by heating the solution. As the temperature rises the ammonia will be released from the water, as shown in the equation below.

$$NH_4OH = NH_3 + H_2O$$

It is also possible to prepare ammonia by heating an ammonium salt with a base.

$$\underset{\text{ammonium sulfate}}{(NH_4)_2SO_4} + \underset{\text{calcium hydroxide}}{Ca(OH)_2} = \underset{\text{calcium sulfate}}{CaSO_4} + \underset{\text{ammonia}}{2NH_3} + 2H_2O$$

Nitrides react with water to form ammonia.

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$$

Ammonia is a colorless, pungent gas which is about one half as heavy as air. It is very soluble in water. At 20 degrees one volume of water absorbs 700 volumes of ammonia. The concentrated solution in water has a density of 0.9 and contains about 28% of the gas.

In the presence of traces of water, ammonia will react with HCl as follows:

$$NH_3 + HCl = \underset{\text{ammonium chloride}}{NH_4Cl}$$

Ammonium hydroxide being a base, one would expect it to unite with acids to form salts. Thus:

$$NH_4OH + HCl = NH_4Cl + H_2O$$
$$2NH_4OH + H_2SO_4 = (NH_4)_2SO_4 + 2H_2O$$

All ammonium salts decompose on heating but all do not release ammonia. However, any ammonium salt heated with a strong base releases ammonia which can be recognized by its odor or its effect on wet red litmus paper, which will turn blue, when it is in contact with ammonia vapors.

$$NH_4Cl + NaOH = NaCl + NH_4OH$$
$$NH_4OH = NH_3 + H_2O$$

Insoluble silver compounds dissolve in ammonium hydroxide. Thus, silver chloride reacts as follows:

$$AgCl + 2NH_4OH = Ag(NH_3)_2Cl + 2H_2O$$

The same is true of copper. If ammonium hydroxide is added to a cupric salt, a precipitate of cupric hydroxide is first formed. As more ammonium hydroxide is added the precipitate goes into solution forming a beautiful blue solution which, in the case of cupric sulfate, is $Cu(NH_3)_4SO_4$ and in the case of cupric chloride, $Cu(NH_3)_4Cl_2$. The formation of this blue color is a test for copper compounds.

Ammonia is used in the preparation of nitric acid, for refrigeration, and fertilizers. Ammonium hydroxide is used by the electroplater in many solutions, and also to adjust the pH of his solutions.

Nitrogen and hydrogen combine to produce ammonia. Haber made this process commercially successful in 1913. The reaction is as follows:

$$N_2 + 3H_2 = 2NH_3$$

At ordinary temperatures, the union of the two gases to form ammonia is very slow. With the increase in temperature, the reaction speed increases up to a maximum and then decreases. If a temperature above 700°C is reached, the reaction is reversed and all the ammonia will decompose to form nitrogen and hydrogen. Haber discovered, however, that when the pressure in the system was increased, the two elements combined to a greater extent. If a temperature of 500°C is used and a pressure of 200 atmospheres (one atmosphere equals 14 lb per sq in.), some ammonia is formed which is absorbed in water. The remaining gases go back into the reacting cham-

ber again. The speed of this reaction is increased if certain catalysts such as iron, uranium, etc., are present. The Claude process for the production of ammonia operates at a pressure of 1000 atmospheres, producing a higher yield of ammonia. The hydrogen used in these processes is generally made from water gas which is a mixture of hydrogen and carbon monoxide. The carbon monoxide is removed by liquefaction. Nitrogen is taken from the air.

It has been mentioned before that in the union of nitrogen and hydrogen the conditions can be altered so that the reaction is reversed, i.e., the ammonia is decomposed to form nitrogen and hydrogen. This is true of other reactions which have been encountered previously, for instance, the formation of ammonium hydroxide from ammonia and water. We can prove this by an interesting test. Let us introduce pure ammonia into a container in which there is an iron compound acting as a catalyst. After keeping the whole at 500°C for a few hours, let us analyze the product. It will be found that some of the ammonia has disappeared and some nitrogen and hydrogen was formed. What does this mean? It simply means that the ammonia has decomposed into nitrogen and hydrogen. If this experiment is repeated it will be found that again the same amount of ammonia will decompose, producing the same amount of nitrogen and hydrogen. After this definite amount of ammonia had decomposed no more nitrogen and hydrogen are formed. It can be proved that ammonia is still decomposing but, at the same time, nitrogen and hydrogen are combining to produce ammonia, and, as fast as the ammonia decomposes, the nitrogen and the hydrogen are united to form more ammonia. This is called an equilibrium reaction. In this reaction a catalyst was present. A catalyst shortens the time interval for a chemical reaction to reach equilibrium, but it

does not change the percentage composition at that equilibrium.

At different temperatures equilibrium mixtures of different composition are produced. In the case of ammonia, the lower the temperature the higher the yield of ammonia, without considering the time factor. If the interval of time is also taken into account, the best yield is obtained at 500° C, while at 700° C, no ammonia is obtained. With any given catalyst, the higher the temperature up to a point the quicker the equilibrium will be attained.

The speed of a chemical reaction may be increased by increasing the concentrations of interacting materials or by increasing the temperature. As a general rule, an increase of 10°C doubles the speed of a chemical reaction.

Nitric acid is a very important material to the chemist and to the electrochemist. It is used in the preparation of other chemicals and in the manufacture of explosives and fertilizers. It is made from nitrates which are deposited in Chile and, synthetically, from the oxides of nitrogen. In electroplating, it is used to make bright dips and as an ingredient in many specific formulae.

If sulfuric acid is mixed with a nitrate, e.g., sodium nitrate, the result is as follows:

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$

It is also possible to oxidize nitrogen in the presence of an electric arc as follows:

(1) $N_2 + O_2 = 2NO$

(2) $2NO + O_2 = 2NO_2$

(3) Hot $H_2O + 3NO_2 = 2HNO_3 + NO$

Another process, known as Oswald ammonia oxidation process, consists of oxidizing ammonia with oxygen as follows:

$$(1)\ 4NH_3 + 5O_2 = 4NO + 6H_2O$$
$$(2)\ 2NO + O_2 = 2NO_2$$
$$(3)\ 3NO_2 + H_2O = 2HNO_3 + NO$$

This method uses platinum as a catalyst. Most of our nitric acid is made by this process.

Nitric acid is a colorless liquid having a density of 1.52 and a boiling point of 86°C. Many times nitric acid solutions turn a red brown color due to the fact that they slowly decompose into oxides of nitrogen and these, when dissolved, produce the characteristic color of nitric acid. Nitric acid is a powerful oxidizing agent. Oxides react readily with nitric acid forming water and nitrates.

$$\underset{\text{cupric oxide}}{CuO} + 2HNO_3 = \underset{\text{cupric nitrate}}{Cu(NO_3)_2} + H_2O$$

Nitric acid reacts with hydrochloric acid producing water, nitric oxide, and free chlorine.

$$HNO + 3HCl = 2H_2O + NO + 3Cl$$

This mixture of nitric acid and hydrochloric acid is called aqua regia and will dissolve many of the inert or noble metals such as gold and platinum. This mixture is used by platers in making up gold solutions.

The salts of nitric acid with bases are called nitrates. Thus:

$$NH_4OH + HNO_3 = \underset{\text{ammonium nitrate}}{NH_4NO_3} + H_2O$$

Many oxides dissolve in nitric acid, for instance:

$$\underset{\text{ferrous oxide}}{FeO} + 2HNO_3 = \underset{\text{ferrous nitrate}}{Fe(NO_3)_2} + H_2O$$

Nitric acid dissolves all metals except noble ones such as gold and platinum. Another reaction which is characteristic of nitric acid is as follows:

$$\underset{\text{magnesium carbonate}}{MgCO_3} + 2HNO_3 = \underset{\text{magnesium nitrate}}{Mg(NO_3)_2} + H_2O + CO_2$$

As the nitrates of all metals are soluble, it will be impossible to precipitate a metallic nitrate. A nitrate generally decomposes on heating as follows:

$$\underset{\text{mercuric nitrate}}{2Hg(NO_3)_2} = \underset{\text{mercuric oxide}}{2HgO} + 4NO + 3O_2$$

However, sodium and potassium nitrate react somewhat differently.

$$2KNO_3 = 2KNO_2 + O_2$$

Many times the chemist desires to test for different radicals. A test for the chloride radical has already been given, and here is a test for the nitrate group. From the reasoning above, that is, that all nitrates are soluble, one would not expect to get a precipitate when testing for a nitrate. However, if a characteristic color can be obtained, it will serve just as well for identification. If a solution of ferrous sulfate ($FeSO_4$) is added to a solution containing the nitrate radical and then concentrated sulfuric acid is added so that two layers of solutions appear, a dark brown ring will form between the ferrous

sulfate solution and the sulfuric acid solution. This test is very delicate and the student may not have success in obtaining the ring the first time. The brown product is $FeSO_4 \cdot NO$. If on the addition of dilute sulfuric acid to the solution, reddish-brown oxides of nitrogen escape, the solution contains a nitrite (NO_2) and not a nitrate (NO_3).

Nitrogen can be made to combine with hydrogen as has been seen before. Ammonia can be converted into ammonium salts or oxidized to nitric acid. The latter can be used to produce nitrates. Some of these processes will be discussed.

Calcium carbide (a compound of calcium and carbon) can be made by heating coke with lime in an electric furnace. Now if nitrogen is passed over this carbide at about 1100°C. cyanamide is formed which can be treated with steam under pressure to yield ammonia. The reactions are as follows:

$$CaCO_3 = CaO + CO_2$$
$$3C + CaO = \underset{\text{calcium carbide}}{CaC_2} + CO$$
$$CaC_2 + N_2 = \underset{\text{calcium cyanide}}{CaCN_2} + C$$
$$CaCN_2 + H_2O = CaCO_3 + 2NH_3$$

This is known as the cyanide process.

If air is passed through an electric arc, at 3000–3500°C, approximately 1% of the air is converted into nitric oxide, (NO). If this is cooled, nitrogen dioxide (NO_2) is formed. If NO_2 is bubbled through water, nitric acid is produced. This can be represented as follows:

(1) $N_2 + O_2 = 2NO$
(2) $2NO + O_2 = 2NO_2$
(3) $H_2O + 3NO_2 = 2HNO_3 + NO$

The gaseous material must be cooled quickly in order that the nitrogen compounds formed do not decompose. This is known as the direct process.

Nitrogen forms several oxides. These are: nitrous oxide (N_2O), nitric oxide (NO), nitrogen dioxide (NO_2), nitrogen trioxide (N_2O_3), and nitrogen pentoxide (N_2O_5). The last two are unstable compounds and are not of commercial importance. Nitric oxide is a colorless gas slightly soluble in water. It can be prepared by the action of dilute nitric acid on copper.

$$8HNO_3 + 3Cu = 2NO + 3Cu(NO_3)_2 + 4H_2O$$

In making nitric oxide in the laboratory it will be noted that a red brown gas first appears and after this is removed, a colorless gas is produced. This is explained by the fact that the nitric oxide unites with the oxygen in the air to produce nitrogen dioxide.

$$2NO + O_2 = 2NO_2$$

Nitrogen dioxide may be prepared by heating the nitrate of any heavy metal, thus:

$$2Hg(NO_3)_2 = 2HgO + O_2 + 4NO_2$$

It can also be prepared by the reaction of concentrated nitric acid and copper.

$$4HNO_3 + Cu = Cu(NO_3)_2 + 2H_2O + 2NO_2$$

It will be noted that dilute nitric acid, acting on copper, produces nitric oxide, while concentrated nitric acid, gives nitro-

gen dioxide. If the temperature of nitrogen dioxide is lowered to 20°C a colorless product is formed which is nitrogen tetroxide (N_2O_4). This will be converted completely back into nitrogen dioxide at 154°C. If the temperature is raised above 620°C, the nitrogen dioxide will decompose into nitric oxide and oxygen. Thus:

$$\underset{\text{Colorless}}{N_2O_4} \rightleftharpoons \underset{\text{Brown}}{2NO_2} \rightleftharpoons \underset{\text{Colorless}}{2NO} + O_2$$

For each temperature there is a definite ratio between the products formed. Nitrogen dioxide unites with water to form nitric and nitrous acids.

$$H_2O + 2NO_2 = HNO_3 + HNO_2$$

Priestley prepared nitrous oxide (N_2O), in 1772, by reducing nitric oxide with moist iron filings. For many years it was thought to be a poisonous material, but was later proved to be non-poisonous and to act as an anesthetic. When a person breathes in larger amounts of this gas he has a tendency to laugh, therefore, it is called "laughing gas." Nitrous oxide is used by dentists when extracting teeth. It can be made by heating ammonium nitrate, but care must be taken that this salt is not heated to too high a temperature, as it may explode with terrific violence. Thus:

$$NH_4NO_3 = 2H_2O + N_2O$$

If a mixture of nitric oxide and nitrogen dioxide is cooled to −21°C, a blue liquid is formed which is nitrogen trioxide. This will decompose, if the temperature is raised.

$$NO_2 + NO = N_2O_3$$

Nitrogen pentoxide (N_2O_5), a white solid, is the anhydride of nitric acid and can be prepared by removing water from nitric acid.

$$2HNO_3 = H_2O + N_2O_5$$

When a certain material is dissolved in a solvent, for instance, sugar in water, certain changes take place. The boiling point is raised a definite amount and the freezing point is lowered a definite amount. Examples of these have been previously given. If, instead of sugar, a gram molecular weight of sodium chloride is dissolved in water, instead of getting the normal increase of the boiling point or lowering of the freezing point a result is obtained which, in either case, is about twice the calculated amount. This shows that salt and sugar are two different types of materials. Let us investigate this difference further. If the sugar solution is introduced into a glass container which contains two electrodes connected in series with an ordinary lamp and a current applied, the lamp will not glow. This simply means that the solution does not conduct the current. If the sodium chloride solution is substituted for the sugar solution the lamp at once begins to burn. Whenever a solution is used in which the raise of boiling point and lowering of freezing point are abnormal, the lamp will burn. It would be rather logical to assume that the solutions which are abnormal in respect to the raising of their boiling points or lowering of their freezing points will conduct electric current. Acids, bases and salts behave the same way as sodium chloride, and since the raise of boiling point and lowering of freezing point depend on the number of dissolved particles, it can be said that acids, bases, and salts undoubtedly break up when dissolved so that the resulting number of particles of the solute are greater than the

theoretical value. For this reason, the boiling point is increased, the freezing point is decreased to a greater extent than the theoretical value, and the solution conducts the electric current. If solid silver nitrate is added to solid sodium chloride (no water whatsoever present) no reaction results. In aqueous solution, a white precipitate of silver chloride would be formed but in solid state no white precipitate of silver chloride is produced. However, if the silver nitrate is dissolved in water and sodium chloride is separately dissolved in water and the two solutions mixed immediately, a white precipitate forms according to the equation

$$AgNO_3 + NaCl = \underset{\text{precipitate}}{AgCl} + NaNO_3$$

In this case, the silver has a tendency to break away from the nitrate radical and the sodium has a tendency to leave the chloride. The silver thus produced is entirely different from metallic silver and the sodium is quite different from metallic sodium. The same can be said about the chlorine present. Let us look at the properties of these elements.

Properties of Free Element	Properties of Combined Element
Sodium	*Dissolved Sodium*
A silver colored metal which is very active. Combines with water to produce sodium hydroxide. $2Na + 2H_2O = 2NaOH + H_2$ It has a melting point of 97.5° and a specific gravity of 0.97.	Colorless; will not react with water and cannot be obtained in the free state.

Properties of Free Element	Properties of Combined Element
Chlorine	*Combined Chlorine*
A greenish yellowish gas, poisonous, moderately soluble in water as follows: $Cl_2 + H_2O = HCl + HOCl$ Can be used as an oxidizing agent as follows: $2Sb + 3Cl_2 = 2SbCl_3$	Colorless, odorless and non-poisonous (in fact used for food in many cases). It cannot be used as an oxidizing agent.

From the above table, it can be seen that there is quite a difference between the free element and the combined element. We also see that all dissolved compounds do not act the same way as, for instance, salt will conduct an electric current while sugar will not. Substances which, in solution, conduct electric current are called electrolytes and solutions which do not conduct an electric current are called non-electrolytes. One can assume, in all cases, that the molecules of electrolytes break up into two or more parts that are free to move in the solution, and are called ions.

Arrhenius suggested the theory of ionization in 1887. This theory assumes the following:

1. Certain substances, when dissolved in certain solvents, break up into small particles called ions.
2. These ions are either positively or negatively charged.
3. The sum of the positive charges equals the sum of the negative charges.

We shall discuss these three points in the order given.

1. It will be noted that certain substances, but not all, will dissolve in certain solvents. For instance, sugar can be dis-

solved in water, but it does not break up, while salt dissolves in water and does break up into small particles called ions. If there is an abnormal raising or lowering of the boiling point or freezing point respectively, ionization takes place.

2. Ions have a positive (+) or negative (−) charge. It is known that unlike charges attract while like charges repel each other. Thus, a positive electrode will collect negative particles. A negative electrode, on the other hand, will collect positive particles. A positive electrode will repel or push away positive particles, while a negative electrode will push away or repel negatively charged particles.

3. Using the ionization theory, one can write equations in a somewhat different manner. Thus, for sodium chloride uniting with silver nitrate:

$$\begin{aligned} &AgNO_3 = Ag^+ + NO_3^- \\ &+ NaCl = Cl^- + Na^+ \\ &\qquad\qquad \downarrow \qquad \Downarrow \\ &\downarrow AgCl \qquad Na^+NO_3^- \end{aligned}$$

This reaction can also be written:

$$Ag^+NO_3^- + Na^+Cl^- = \downarrow AgCl + Na^+NO_3^-$$

The first equation shows that silver nitrate breaks up into positively charged silver ion and negatively charged nitrate ion, while the sodium chloride forms positive sodium ion and the negative chloride ion. These ions, in turn, unite to give silver chloride and sodium nitrate. The last equation gives the whole reaction in one step. It will be noted that no positive or negative charge is written above the AgCl. This is because the AgCl is insoluble and precipitates out of solution, but the com-

pounds that stay in solution have a positive and negative charge. This type of equation is called ionic equation.

Sodium chloride ionizes as follows:

$$NaCl = Na^+ + Cl^-$$

If one could add a negative charge called electron to the sodium ion, an atom of sodium would be produced as follows:

$$Na^+ + \theta = Na$$

(Theta, θ, is a Greek letter used to designate one negative charge of electricity that is called electron.) Thus Na^+ has a surplus of one positive charge. It has been found that positive charges do not migrate because of their great bulk but negative charges move about due to their light weight. When it is said that a surplus of one positive charge is present as in the case of Na^+, this means that one negative charge has been lost. If an excess of one positive charge is present, as in the case of Na^+ and one negative charge or one θ is added, we will get a neutral atom again because the negative charge neutralizes the excess positive charge. The equation can be written thus:

$$Na^+ + \theta = Na^\circ$$

If an electron is removed from a Na atom, a sodium ion Na^+ will result.

$$Na^\circ - \theta = Na^+$$

In the first case, one electron was added to neutralize the excess positive charge. In the second case, one negative charge was taken away to produce a sodium with a positive charge.

The only difference between sodium ion and a sodium atom is the absence or presence of a negative charge of electricity. The sodium ion, having a positive charge, will go to the negative electrode or cathode. Chlorine, on the other hand, when in the form of a chloride ion having a negative charge, will go to the positive electrode or anode. There are two different products of electrolysis. These are called primary and secondary products. A primary product is obtained when the material decomposed is released without further chemical reaction taking place. A good example of this is the electrolysis of copper chloride. Dissolved copper chloride ionizes to produce copper ions and chloride ions. The copper ions being positively charged migrate to the cathode and there the copper ion is reduced to metallic copper and can be obtained as such from the solution. The choride ions migrate to the anode and are neutralized to chlorine. Thus copper chloride is decomposed into its component parts and the copper and the chlorine are recovered as such. The ionic equation of dissolving copper chloride is as follows:

$$CuCl_2 = Cu^{++} + 2Cl^-$$

This means that copper in order to become metal copper must gain two negative charges of electricity or two electrons. On the other hand, two chloride particles are present, which must lose two electrons in order to become gaseous chlorine. How can this be brought about? It will be recalled that the anode has an excess of positive charges which is another way of saying that it lacks negative charges while the cathode has an excess of negative charges. Thus, it can be seen that the anode will absorb negative charges while the cathode will give up negative charges. Now copper, being positive, migrates to the cathode which, having an excess of negative charges, gives up two electrons as follows:

$$Cu^{++} + 2\theta = Cu^{o}$$

Thus, we obtain metallic copper at the cathode. In the same manner the anode, being positive, attracts the chlorine ions which are negative. In this case the chlorine gives its two electrons to the anode and becomes gaseous chlorine:

$$2Cl^{-} - 2\theta = Cl_2$$

Thus, ions carry charges to the cathode and to the anode, and electrolysis depends upon this flow of electric charges. The electrons enter at the cathode, pass through the solution, go over to the anode and then pass from the metallic conductors through the generator and back again to the cathode. This will be clear from Fig. VI.

When the products liberated during electrolysis of aqueous solutions react with water, secondary products will be obtained. If an aqueous solution of sodium chloride is electrolyzed, the sodium ions go to the cathode and gain an electron and become free sodium metal. However, sodium is very reactive with water and immediately the following reaction takes place:

$$2Na + 2H_2O = 2NaOH + H_2$$

Therefore, at the cathode, instead of sodium metal, hydrogen is produced. At the anode the chlorine gives up its charge and forms chlorine gas. In this case, hydrogen, sodium hydroxide, and chlorine are the products of electrolysis. Such secondary reactions will occur when potassium, sodium, barium, strontium, and calcium salts are electrolyzed in the presence of water. Secondary products are also formed when the electrolyte contains negative ions composed of more than one element, such as a nitrate, or sulfate radical. In this case, the secondary prod-

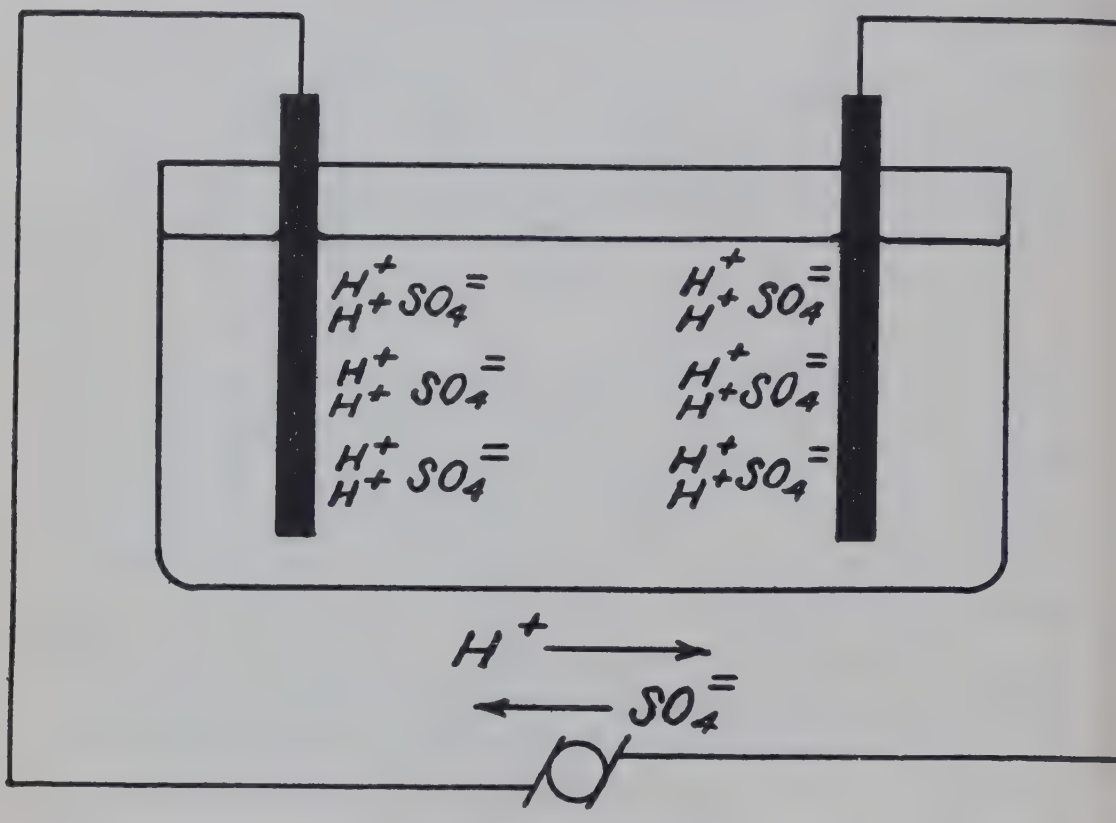


FIG. VI

ucts, of course, will be formed at the anode, instead of at the cathode. The electrolysis of copper sulfate is a good example. When copper sulfate is dissolved in water, the following ionization takes place:

$$CuSO_4 = Cu^{++} + SO_4^{--}$$

If this solution is electrolyzed, the copper ion migrates to the cathode and is discharged as metallic copper. The sulfate ions

are attracted to the anode and, on being liberated, react with the water as follows:

$$2SO_4^{--} + 2H_2O = 2H_2SO_4 + O_2$$

The sulfate ions are very reactive. They unite with the hydrogen in water to produce sulfuric acid and oxygen. Thus, the final products are copper at the cathode, oxygen at the anode, and sulfuric acid in solution. In all these electrolyses, insoluble electrodes, such as platinum electrodes, were used.

The electron is the smallest part of negative electricity that can be transferred from one atom to another. It has a maximum weight of $\frac{1}{1845}$ of that of the hydrogen atom. The positive charge of electricity, which is called proton, is equivalent in weight to a hydrogen atom, that is, it is approximately 1845 times larger than the electron.

QUESTIONS

1. What is meant by a reversible reaction?
2. How does a rise in temperature affect the speed of a chemical reaction?
3. 10 cc of a 0.1 normal sodium hydroxide solution neutralizes 25 cc of nitric acid solution of unknown normality. What is the normality of the nitric acid solution?
4. How many grams of nitric acid can be made from 10 grams of sodium nitrate?
5. How could you prove the following to be electrolytes or non-electrolytes: Nickel sulfate; sugar; sulfuric acid; starch?
6. Write the equation for barium chloride uniting with sulfuric acid in a chromium plating bath.
7. Define and give two examples of a positive ion and a negative ion.

8. Give three assumptions of the theory of ionization.
9. Compare the properties of a chlorine atom and a chlorine ion.
10. What is the approximate size of the electron?
11. Define electrolysis.
12. Does oxidation or reduction occur at the cathode?
13. How much sodium hydroxide can be prepared from 20 grams of sodium chloride?
14. 15 cc of a 0.25 normal solution of sodium hydroxide neutralizes 10 cc of an unknown sulfuric acid solution. What is the normality and molarity of the sulfuric acid solution?

CHAPTER VIII

Ionic Reactions; Compounds of Sodium and Potassium

In the last chapter, the compounds of nitrogen were studied and methods for their production were given. In this chapter, ionic reactions are illustrated in detail and sodium and potassium compounds are studied. As has been discussed before, compounds are roughly divided into two different types: Those which ionize and conduct electric current (called polar compounds) and those which do not ionize and, therefore, do not conduct an electric current (called non-polar compounds). Examples of polar compounds are sodium chloride, nickel sulfate, and sulfuric acid. Examples of non-polar compounds are carbon tetrachloride, trichlorethylene and sugar. There is not a sharp distinction between the two classes; for instance, weak bases and weak acids fall between the two classes. Also, concentrated sulfuric acid is not ionized. Many other discrepancies are found.

Acids and bases are polar compounds. Upon examination, it will be found that all acids contain hydrogen. On the other hand, compounds that contain hydrogen are not necessarily acids. If a material contains hydrogen and ionizes in solution to produce hydrogen ions (H^+), the compound is an acid, but if no hydrogen ion is produced the material is not an acid. Therefore, an acid can be defined as a compound which, dissolved in water, produces hydrogen ions. Acids can be divided into different groups depending upon how many hydrogens are

present. Thus, monobasic acids release one hydrogen ion. Examples are HCl and HNO_3. Dibasic acids yield two hydrogen ions per molecule. An example is H_2SO_4, while tribasic acids yield three hydrogen ions, for instance, H_3PO_4.

A base may be defined as any material which produces hydroxyl ions in a water solution. Bases can be also divided into classes. A monoacid base yields one hydroxyl ion per molecule. KOH and NaOH are examples. Magnesium hydroxide, $Mg(OH)_2$, is a diacid base and aluminum hydroxide $Al(OH)_3$, is a triacid base. Salts can be defined as the products of neutralization of an acid by a base.

If the water solutions of some acids and bases are investigated, it will be found that they are rather poor conductors of electric currents. What can be the reason for this? It will also be noted that these substances are not as active as those which conduct a current very readily. A good example of one of the poor electrolytes is acetic acid. This will not attack metals as readily as will hydrochloric acid. The answer is that the acetic acid does not produce as many hydrogen ions as does hydrochloric acid. Acetic acid is called a weak acid. Another good example of weak acids is sulfurous acid. When dissolved in water, it forms some but not many hydrogen ions according to the equation:

$$H_2SO_3 \rightleftharpoons 2H^+ + SO_3$$

On the other hand, it is known that this acid is soluble in water. What becomes of that part which does not give hydrogen ions? The hydrogen ion simply unites with the sulfite ions to produce molecular H_2SO_3, that is, most of the sulfuric acid is in the molecular form and not in the ionic form. Ammonium hydroxide is a weak base because it produces, when dissolved

n water, comparatively few hydroxyl ions. This may be repre-sented as follows:

$$NH_4OH \leftrightharpoons NH_4^+ OH^-$$

To show that it is a weak base the arrow pointing to NH_4OH s heavy while the arrow pointing to the disassociating products s light. Thus, one sees that most of the ammonium hydroxide s in the molecular state.

When an acid and a base come together, neutralization occurs. This reaction may be considered practically complete. The essential reaction of neutralization is the combination of a hydrogen ion of the acid with a hydroxyl ion of the base, forming water. The driving force results from the fact that the water which is formed is removed from the zone of action and does not disassociate to form hydrogen ions or hydroxide ions again. Perhaps an example will make this clear. When HCl is neutralized by NaOH the following reaction takes place:

$$HCl \rightleftharpoons H^+ + Cl^-$$

$$NaOH \rightleftharpoons \underset{\Downarrow\Uparrow}{OH^-} + \underset{\Downarrow\Uparrow}{Na^+}$$

$$\underset{H_2O}{} \qquad \underset{NaCl}{}$$

From the above it can be seen that hydrochloric acid disasso-ciates into hydrogen and chlorine ions. The reverse, however, s also true, that is, hydrogen ions and chlorine ions unite to form hydrochloric acid. Again, sodium hydroxide dissociates nto sodium and hydroxyl ions. The sodium ion unites with he chloride ion to form NaCl, the hydrogen ion unites with he hydroxyl ion to form water, and these reactions are also

reversible, but in the case of water, the dissociation is very slight and may be considered as non-existing. Therefore, the reaction must go to the right. This can also be written as follows:

$$H^+ + Cl^- + Na^+ + OH^- \rightleftharpoons Na^+ + Cl^- + H_2O$$

In every case, the solution as a whole is electrically neutral as the number of positive ions equals the number of negative ions.

Nearly all reactions occurring in water are ionic reactions and are instantaneous, that is, they reach the end point at once. Just what the end point will be depends upon the ionic equilibrium. This is determined by the properties of the substances under consideration. For instance, if aqueous solutions of potassium chloride and sodium sulfate are mixed, the reaction does not necessarily form potassium sulfate and sodium chloride because there is no driving action between these compounds: there are potassium ions, sulfate ions, sodium ions and chloride ions in the mixture. On the other hand, if potassium chloride is added to silver nitrate the reaction will go to completion because silver chloride will form which, being insoluble, precipitates from the solution. These two reactions can be represented as follows:

1. $K^+ + Cl^- + 2Na^+ + SO_4^= \rightleftharpoons K^+ + Cl^- + 2Na^+ + SO_4^=$
2. $K^+ + Cl^- + Ag^+ + NO_3^- \rightleftharpoons K^+ + NO_3^- + AgCl\downarrow$

The last reaction goes to completion because the silver ion and the chloride ion unite to form molecular silver chloride, and are removed from the zone of action.

Every ionic reaction is reversible to a certain extent but the

reversibility, in some cases, is so slight that it is disregarded and the reaction to the right is assumed to be complete. Thus, for the formation of silver chloride, we can write:

$$Ag^+ + Cl^- \rightleftharpoons AgCl$$

It is true that silver chloride is very slightly soluble in water and, therefore, there is an equilibrium between the ions and molecular silver chloride, but the dissociation of the latter is very slight. The amount of silver chloride forming silver and chloride ions can be further decreased by adding either silver or chloride ions. Ionic reactions can be made to go to completion under certain conditions. Ionic reactions go to completion if two oppositely charged ions produce insoluble materials or components which are slightly ionized. Types of reactions which go to completion can be enumerated as follows:

1. A gas is formed which is insoluble in the solution, for example,

$$2HCl + Na_2CO_3 = 2NaCl + H_2O + CO_2$$

2. Insoluble precipitate is formed, for instance:

$$BaCl_2 + Na_2SO_4 = \downarrow BaSO_4 + 2NaCl$$

$BaSO_4$ is insoluble in water.

3. One of the reaction products is slightly ionized. The best example of this is the neutralization of an acid with a base, producing water.

The solubility of various compounds in water is of great interest to the electroplater. Some general rules of solubility are as follows:

1. All nitrates, acetates, and chlorates are soluble in water.

2. All sodium, potassium, and ammonium compounds ar soluble in water.

3. All sulfates are soluble in water except barium sulfate lead sulfate, and calcium sulfate.

4. All chlorides are soluble in water except those of silver mercury, and lead.

5. All oxides and hydroxides are insoluble in water excep ammonium hydroxide, sodium hydroxide, potassium hydrox ide, and barium hydroxide. Calcium hydroxide is slightly soluble.

6. All carbonates are insoluble in water except those of sodium, potassium and ammonium.

It was previously explained that valence is the ability of one element to combine with another element. It was also stated that valence could be represented by supposing that each element has a certain number of hooks or hands with which it can join with another element. Let us now reconsider these statements, bringing in the electric charge. It is known, for instance, that some elements have a positive and others have a negative charge and also, for two elements to unite, one must be positively charged and the other negatively charged. Instead of putting hands, hooks, or arms on the elements, the valence can be designated by using the proper number and type of charges. Thus, hydrogen has a valence of one and is positive. This can be written H^+. Sodium, in like manner, Na^+. Nickel has two positive charges and can be written Ni^{++}. Aluminum has three positive charges and can be written as Al^{+++}. On the other hand, the non-metals are negative. For instance, chlorine has one negative charge and can be written as Cl^-. Likewise, OH^- and NO_3^-. When chlorine changes from an atom to an ion, it gains one electron as shown below:

$$Cl_2 + 2(\theta) = 2Cl^-$$

However, sodium does not gain a positive charge or proton, when it goes from the atomic into the ionic state. Sodium loses an electron or negative charge and therefore one free positive charge remains on the sodium.

$$Na^{\circ} - (\theta) = Na^{+}$$

In every known reaction, it is always the electron, and not the proton, that is lost or gained. If the metal sodium unites with chlorine to produce sodium chloride, the sodium loses one electron to the chlorine so that the sodium becomes Na^{+} and the chlorine becomes Cl^{-}.

There are a number of ions which will combine with other ions or molecular substances to form complex ions. It is also possible to make complex salts. Thus, if silver chloride is dissolved in ammonium hydroxide, soluble silver ammonium chloride results. In the electroplating industry much use is made of the formation of complex ions because it is generally known that better deposits result when complex ions are present. The cyanides are used to form these complex substances. With zinc the following complex is formed:

$$Zn(CN)_2 + 2NaCN \rightleftharpoons Na_2Zn(CN)_4$$

This material ionizes as follows:

$$Na_2Zn(CN)_4 \rightleftharpoons 2Na^{+} + Zn(CN)_4^{=}$$

It may be seen that no zinc ion is present and zinc could not be deposited, if a current were passed through such a solution. However, the complex ion ionizes slightly to produce two ions as follows:

$$Zn(CN)_4^{=} \rightleftharpoons Zn^{++} + 4CN^{-}$$

Copper cyanide also unites with sodium cyanide forming a compound which has the formula $Na_2Cu(CN)_3$. This ionizes the same way as the zinc compound:

$$Na_2Cu(CN)_3 \rightleftharpoons 2Na^+ + Cu(CN)_3^=$$
$$Cu(CN)_3^= \rightleftharpoons Cu^+ + 3CN^-$$

Silver acts in much the same way:

$$AgCN + KCN \rightleftharpoons KAg(CN)_2$$

This complex can also be formed with other silver compounds:

$$AgCl + 2KCN \rightleftharpoons KAg(CN)_2 + KCl$$

$KAg(CN)_2$ ionizes as follows:

$$KAg(CN)_2 \rightleftharpoons K^+ + Ag(CN)_2^-$$
$$Ag(CN)_2^- \rightleftharpoons Ag^+ + 2CN^-$$

Sodium chloride, NaCl, is a very important salt of sodium and is mined. It has been discussed before in detail.

Sodium carbonate is now made by the "Solvay" process. It originally was made by the LeBlanc method but the former is cheaper and has now supplanted this process. Only the Solvay process will be discussed as the LeBlanc process is obsolete. A saturated solution of sodium chloride is saturated with ammonia and carbon dioxide to form, at first, ammonium bicarbonate which, in turn, reacts with sodium chloride to form sodium bicarbonate. This salt being only partially soluble in the solution, precipitates and the precipitate is heated to form sodium carbonate. The reaction is as follows:

$$NH_4OH + H_2CO_3 = (NH_4)HCO_3 + H_2O$$
$$(NH_4)HCO_3 + NaCl = NaHCO_3 + NH_4Cl$$
$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

The reaction is carried out in large water towers in which are numerous shelves and water traps so that complete mixing is assured. The temperature of the reaction should not go above 35°C. The ammonium chloride, which is produced in the reaction as shown by the second equation, is expensive and cannot be wasted. It is heated with lime so that ammonia is released. The lime is obtained by heating calcium carbonate. The equations are:

$$CaCO_3 = CaO + CO_2$$
$$CaO + H_2O = Ca(OH)_2$$
$$Ca(OH)_2 + 2NH_4Cl = CaCl_2 + 2NH_3 + 2H_2O$$

The carbon dioxide, which is released in the first reaction, is used in the carbonating tower. The calcium hydroxide produced is used for regenerating the ammonia. The end products are sodium carbonate and calcium chloride. Calcium chloride is of very little commercial value. The raw materials are calcium carbonate (limestone) and sodium chloride. Both substances are cheap.

If the reaction is stopped short and the last step is not allowed to take place, the product is sodium, hydrogen carbonate or sodium bicarbonate. Sodium bicarbonate solutions are slightly alkaline. Sodium bicarbonate can be produced from sodium carbonate by saturating a water solution of sodium bicarbonate with carbon dioxide, sodium bicarbonate being precipitated:

$$Na_2CO_3 + H_2O + CO_2 = 2NaHCO_3$$

The reverse reaction will take place if the sodium bicarbonate is heated. Both sodium bicarbonate and sodium carbonate will react with an acid producing salt (NaCl), and carbon dioxide according to the equation below:

$$NaHCO_3 + HCl = NaCl + H_2O + CO_2$$

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2$$

Sodium carbonate can be obtained as a dry powder (amorphous sodium carbonate) or in the crystalline form which is hydrated sodium carbonate. The first has the formula Na_2CO_3 and the second has the formula $Na_2CO_3 \cdot 10H_2O$.

Sodium sulfate, Na_2SO_4, is found in nature as such, but also as a hydrate, $Na_2SO_4 \cdot 10H_2O$, called Glauber's salt. Large amounts of this substance are used in glass making and in the manufacture of certain types of paper. It can be produced by the reaction of sodium nitrate with sulfuric acid.

$$2NaNO_3 + H_2SO_4 = 2HNO_3 + Na_2SO_4$$

Sodium sulfite is obtained by adding sulfur dioxide to a saturated solution of sodium carbonate and then adding a definite amount of carbonate. The reaction equations are as follows:

$$Na_2CO_3 + 2H_2SO_4 = H_2CO_3 + 2NaHSO_3$$

$$Na_2CO_3 + 2NaHSO_3 = H_2CO_3 + 2Na_2SO_3$$

One of the best ways of preparing sodium cyanide is to fuse cyanamide with carbon and sodium carbonate.

$$Ca(CN)_2 + Na_2CO_3 + C = CaCO_3 + 2NaCN$$

The sodium cyanide produced can be dissolved away from the other material, using water as solvent.

Sodium thiosulfate is also known to photographers as hypo and is used to dissolve the unused silver bromide from the developed plates. It can be formed very easily by boiling sodium sulfite with sulfur.

$$Na_2SO_3 + S = Na_2S_2O_3$$

Sodium sulfide is a very soluble sodium salt and can be produced by reducing sodium sulfate with carbon at 900°C.

$$Na_2SO_4 + 2C = Na_2S + 2CO_2$$

Sodium nitrate is obtained from the great saltpeter beds which are in Chile. This is a very important source of nitrogen. It can also be made synthetically.

Sodium nitrite can be obtained from sodium nitrate by heating:

$$2NaNO_3 = 2NaNO_2 + O_2$$

There are three sodium phosphates: monosodium, disodium, and trisodium phosphate. Their formulas are NaH_2PO_4, Na_2HPO_4, and Na_3PO_4, respectively. Each of these is prepared by adding the correct amount of sodium hydroxide to phosphoric acid.

If sodium carbonate is dissolved in water and the resulting solution tested with red litmus, the red litmus will turn blue, indicating a basic reaction. The explanation is that water reacts chemically with certain types of salts to produce acids or bases, as the case may be. Water is very slightly ionized to hydrogen and hydroxyl ions. This slight ionization plays an important

part with certain salts as we will now see. Sodium carbonate consists of a strong base (sodium hydroxide) and a weak acid (carbonic acid). If the sodium ion can find a hydroxyl ion with which to unite, sodium hydroxide will be produced. At the same time, if the carbonate ion can find hydrogen ions with which to unite, carbonic acid will be formed. Sodium hydroxide is a much stronger base (that is, it ionizes more) than carbonic acid is an acid. Thus, one would expect a basic reaction to occur if sodium hydroxide and carbonic acid were formed in solution. This can be written as follows:

$$2H_2O \rightleftharpoons 2H^+ + 2OH^-$$

$$Na_2CO_3 \rightleftharpoons CO_3^{=} + 2Na^+$$

$$\begin{matrix} & & \Downarrow \\ & H_2CO_3 & 2NaOH \end{matrix}$$

From the above equations it will be noticed that hydrogen and hydroxyl ions are formed, the hydrogen ions immediately combining with the carbonate ions to form molecular H_2CO_3, which is only slightly ionized, while the hydroxyl ions do not combine with the sodium ions to form the molecular material, but form ionized sodium and hydroxyl ions. Thus, sodium carbonate reacts strongly basic. This reaction is called hydrolysis. It takes place when a salt of a strong base and a weak acid or a salt of a strong acid and a weak base is dissolved in water. In the first case, an alkaline reaction and in the second case, an acid reaction occurs.

Potassium and sodium compounds are very similar in their reactions. As a general rule it might be stated that potassium salts are more soluble and are more expensive than sodium salts. In nearly every case, the chemical reactions are the same.

Metallic sodium and potassium are obtained by electrolyzing the fused sodium or potassium hydroxide. These metals can

also be obtained by electrolyzing the corresponding chloride instead of the hydroxide. The electrolysis of a fused salt is similar to that of an aqueous solution except that no water is present. The salt is heated until liquid and then a current is passed through. Sodium or potassium is produced at the cathode while oxygen or chlorine is released at the anode. Both of these metals are very soft and have a silver-white luster. They are very active and oxidize in the atmosphere at once. In order to protect these metals from oxidation, they must be placed under a unreactive solution such as kerosene. This prevents the oxygen of the atmosphere from combining with the metals.

If sodium is heated in the air, sodium peroxide (Na_2O_2) is formed. This substance contains one more atom of oxygen than sodium oxide and, for that reason, is a strong oxidizing agent.

As nearly all salts of sodium and potassium are soluble, other methods besides insoluble precipitates for testing of these materials must be used. Bunsen developed a flame test for these materials. Sodium or potassium salts give a characteristic color when placed in the flame. Sodium compounds produce a yellow flame while potassium compounds produce a purple or violent flame.

QUESTIONS

1. Define polar and non-polar compounds.
2. If dry silver nitrate and sodium chloride are mixed, no reaction occurs. Explain.
3. Define valence in terms of electrons.
4. In the determination of sulfate in a chromium plating solution the chemist always adds an excess of barium chloride. Why?
5. How is sodium cyanide made?
6. Would you rather use sodium bicarbonate or sodium carbonate? Explain.

7. How many grams of water are formed when 20 grams of sodium hydroxide unite with an excess of hydrochloric acid?
8. Upon analyzing a certain chromic acid bath, it was found to contain 0.6 ounces per gallon of sulfuric acid. The formula called for only 0.5 ounces per gallon of sulfuric acid. If the tank contained 480 gallons of solution, how much $BaCO_3$ must be added in order to reduce the acid content to the required amount?
9. A plater uses a standard sodium cyanide solution to titrate his nickel solutions. If each cubic centimeter of the reagent equals 0.014 grams of nickel metal, and a 10 cc sample of the bath requires 15 cc of the standard solution, how much nickel metal is present in a liter solution? How much $NiSO_4$; $NiSO_4 \cdot 7H_2O$?
10. In the above problem what is the normality and molarity of the nickel sulfate solution?

CHAPTER IX

The Halogen Family; The Periodic Law; The Structure of the Atom

In the preceding chapter, some reactions as well as sodium and potassium salts were discussed. In this chapter the halogen family is treated and the periodic law of the elements is discussed.

Some elements show similarity or definite relationship of the physical and chemical properties, and are considered as members of a group or family. The halogen family is a good example of this. The four members of this group have all similar properties. Fluorine, chlorine, bromine, and iodine belong to the halogen group; all are non-metals, form negative ions in solution and each has a valence of one. The name of this family, halogen, comes from the Greek and means salt former for the reason that they unite with metals to produce salts.

Hypochlorous acid is a powerful oxidizing agent. It is formed by dissolving chlorine in water.

$$Cl_2 + H_2O = HCl + HOCl$$

Litmus paper turns red in this solution and is then bleached by the action of the compound. If HCl is added to the solution the following reaction takes place:

$$HCl + HOCl \rightleftharpoons H_2O + Cl_2$$

Hypochlorous acid decomposes in sunlight:

$$2HOCl = 2HCl + O_2$$

Hypochlorous acid is a powerful oxidizing agent as shown by the equation:

$$H_2S + HOCl = H_2O + HCl + S$$

It will also oxidize sulfurous acid to sulfuric acid:

$$H_2SO_3 + HOCl = H_2SO_4 + HCl$$

Hypochlorous acid will oxidize iodine to iodic acid as follows:

$$5HClO + I_2 + H_2O = 5HCl + 2HIO_3$$

One of the best ways of preparing hypochlorous acid is by dissolving chlorine in water.

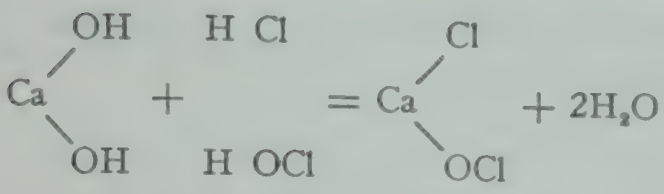
When hypochlorous acid is neutralized, salts are produced which are called hypochlorites. Sodium hypochlorite, NaOCl, sometimes called Javelle water, is made by passing chlorine into sodium hydroxide:

$$Cl_2 + 2NaOH = NaOCl + NaCl + H_2O$$

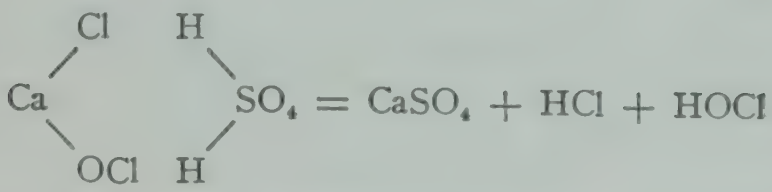
The hypochlorites are unstable compounds. They will oxidize into chlorates if allowed to stand or heated. Thus:

$$3NaOCl = 2NaCl + NaClO_3$$

If chlorine is allowed to react with lime in the dry state, bleaching powders result according to the following equation:



If bleaching powders are acidified, the following reactions take place:



$$HCl + HOCl \leftrightharpoons H_2O + Cl_2$$

Chloric acid is made by the action of dilute sulfuric acid on barium chlorate:

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2HClO_3$$

One of the most important chlorates is potassium chlorate, $KClO_3$. This is formed by passing chlorine into a solution of hot potassium hydroxide.

$$3Cl_2 + 6KOH = KClO_3 + 5KCl + 3H_2O$$

Bleaching is usually an oxidation process. Colored inorganic materials can be made colorless by bleaching with oxygen. Nascent oxygen will oxidize or bleach much faster than molecular oxygen. Nascent oxygen can be obtained from hypochlorous acid:

$$HOCl = HCl + O$$

The nascent oxygen thus produced oxidizes or bleaches. Bleaching powders react as follows:

$$CaCl(OCl) + CO_2 + H_2O = CaCO_3 + HOCl + HCl$$
$$HOCl = HCl + O$$

The carbon dioxide, in the above equation, comes from the atmosphere.

Potassium perchlorate is a very strong oxidizing agent and can be formed by heating potassium chlorate:

$$4KClO_3 = 3KClO_4 + KCl$$

Bromine can be prepared electrolytically. Any soluble bromide, upon electrolysis, will yield bromine. Bromine may also be displaced from bromides by the action of chlorine.

$$2KBr + Cl_2 = Br_2 + 2KCl$$

It may also be prepared by heating potassium bromide and manganese dioxide with concentrated sulfuric acid.

$$2KBr + MnO_2 + 3H_2SO_4 = 2KHSO_4 + MnSO_4 + Br_2 + 2H_2O$$

Bromine is a deep reddish-brown liquid which has a very low boiling point. Therefore, it evaporates readily. It has a very disagreeable odor and will attack the skin tissues. It is moderately soluble in water but is more soluble in alcohol, ether, and carbon disulfide.

Hydrogen bromide may be prepared by the direct combination of hydrogen and bromine.

$$H_2 + Br_2 = 2HBr$$

Hot platinum gauze acts as a catalyst. It may also be prepared by the reaction of phosphoric acid and bromide.

$$NaBr + H_3PO_4 = HBr + NaH_2PO_4$$

Hydrogen bromide is a colorless gas of pungent odor and has an irritating effect on the nostrils. It is quite soluble in water and ionizes to hydrogen ions and bromide ions. Being a typical acid, it readily reacts with metals, metal oxides, and bases. It will precipitate silver from solution as follows:

$$AgNO_3 + HBr = AgBr\downarrow + HNO_3$$

The salts of hydrobromic acid are called bromides. Thus, NaBr is sodium bromide. All bromides are soluble except those of silver, lead, and mercury.

Iodine is a grayish-black solid and if heated forms a violet-colored vapor. One peculiarity of this element is that when heated it passes from the solid to the vapor state without going into the liquid state. This is known as sublimation. Iodine is slightly soluble in water, very soluble in alcohol, carbon disulfide and ether. It can be prepared as follows:

$$2NaI + MnO_2 + 3H_2SO_4 = 2NaHSO_4 + MnSO_4 + 2H_2O + I_2$$

It can also be prepared by displacement with chlorine or bromine.

$$2NaI + Cl_2 = 2NaCl + I_2$$

$$2NaI + Br_2 = 2NaBr + I_2$$

If a small amount of iodine is brought into contact with a starch solution, a deep blue color is produced. This is used as a test for iodine.

Hydroiodic acid (HI) may be prepared in a manner similar to hydrobromic acid:

$$KI + H_3PO_4 = HI + KH_2PO_4$$

It can also be prepared as follows:

$$2P + 3I_2 + 6H_2O = 2H_3PO_3 + 6HI$$

It is a colorless gas and is quite soluble in water, producing hydrogen and iodide ions. It is a strong acid, which produces a precipitate with the salts of silver, lead, and mercury. This means, of course, that silver, lead and mercuric iodides are insoluble in water.

The first member of this group, fluorine, is the most active, and therefore, very hard to prepare in the free state. Hydrogen fluoride is prepared as follows:

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$$

Hydrofluoric acid is important because it will react with silica and silicates. Common glass is a mixture of sodium and calcium silicates and silicon dioxide, and hydrofluoric acid will dissolve these materials. Therefore, it is essential that this acid is stored in rubber or paraffin bottles. The action of fluoric acid on glass can be represented by three equations:

1. $SiO_2 + 4HF = SiF_4 + 2H_2O$
2. $Na_2SiO_3 + 6HF = SiF_4 + 3H_2O + 2NaF$
3. $CaSiO_3 + 6HF = SiF_4 + 3H_2O + CaF_2$

There are many other compounds of fluorine but as they are not too important they are not discussed here.

The halogens may be arranged in the order of their activity. Thus, fluorine is the most active, chlorine next, bromine next and iodine last. This arrangement also indicates that bromine will displace iodine from its compounds and chlorine will, in turn, displace bromine and fluorine will displace chlorine.

It was mentioned that certain elements are similar to one another and fall into groups or families. About the year 1865, Newland observed that if he arranged the elements according to increasing atomic weights in rows of eight members nearly every eighth element exhibited properties similar to those of the one above it. This was also known as the law of octaves. It worked for some of the elements but not for all of them. Mendelejeff, in 1869, made a better classification. He also arranged the elements in the order of increasing atomic weights, but he placed hydrogen by itself in group one. Next came helium and in the same period seven other elements. The first period consists of helium through flourine. The second period consist of elements from neon to chlorine. Now neon is similar to helium in that it is an inert gas. Sodium is like lithium, etc., until we come to the last which is chlorine, and is, as was learned in the previous chapter, similar to fluorine. The third period contains eighteen elements beginning with argon and ending with bromine. In this period, the first eight elements, argon through manganese, are placed directly under periods one and two. This takes care of twenty-five elements. Then iron, cobalt, and nickel are placed in group eight, then period three continues by placing copper under potassium and ending with bromine, which is placed under chlorine. Periods four and five can be obtained in a similar manner. At the time that Mendelejeff put forth his theory there were many blank places in the periodic system. He suggested that elements are missing there which were not as yet discovered. This has proven to be true as most of the missing elements have been discovered since. In three

instances, in the case of argon and potassium, cobalt and nickel, tellurium and iodine, it has been necessary to reverse the order in which the atomic weight placed the elements so as to bring the elements into their proper family. According to Mendelejeff, the properties of the elements are functions of their atomic weights.

The periodic system gives the chemist an idea of the general properties of elements. Take the halogen family for instance. If one knows the properties of chlorine some of the properties of fluorine, bromine and iodine will also be known.

It is possible to predict missing elements and their properties. This has aided the scientist in many fields and has led to the identification of elements which would otherwise have been very hard to accomplish.

There are objections, however, to the periodic system. Hydrogen does not have a definite placing. Tellurium is heavier than iodine, and if placed in this order iodine would be out of its family as would tellurium. The same holds for cobalt and nickel, argon and potassium. No quantitative relations are obtained. Manganese should not be grouped with the halogens. Finally, the system has the serious defect of not accounting for the varying valences of some elements.

Moseley found in 1912 that the chemical properties of the elements are periodic functions of their atomic numbers. He allowed cathode rays which consist of a stream of electrons to strike a definite substance, producing X-rays. Moseley used different metals as anti-cathodes of the X-ray bulb and photographed the X-rays produced and then calculated their wave lengths. He found that the wave lengths decreased in a quantitative way as the atomic weights increased. Moseley discovered an almost linear relationship between the X-ray frequencies and the square of the atomic numbers of a series of elements. Thus, Moseley used the atomic numbers instead of the atomic

weights for the classification of the elements. The atomic numbers are all whole numbers and approximately half the atomic weight, and represent the number of protons in the nucleus of the atom. In this new classification the elements fall into nine groups. The first and second periods are short periods while the third period is a long one. It will be noticed that a long period always has three elements which are called transition elements. These always fall into group eight. Thus iron, cobalt, and nickel are transition elements in the third period.

From a study of the periodic system it will be noted that the groups generally indicate the valence, thus, for groups one, hydrogen has a valence of one, lithium a valence of one, etc. Group two, beryllium, magnesium, calcium, and zinc each has a valence of two, while in the third group, aluminum has a valence of three. In the first two periods, the members of groups six and seven are very active non-metallic elements. In regard to valence—toward oxygen—the maximum valence of the different groups is seven, but toward hydrogen and chlorine the valence rises only to four in group four and then decreases to one. In groups one and two there are very active metals. In the middle of a period we should have a transition element or a substance which can act as both a metal and a non-metal. In general, the most active metals are in group one and the most active non-metals are in group seven. Metals which can act either way appear in the middle. Another way of stating this is to say that elements being most electropositive occur in group one, while elements being most electronegative appear in group seven.

Now the structure of the atom will be considered. Positive and negative particles which make up the atom have been discussed, but nothing has been said concerning their arrangement. According to the latest views of science an atom is com-

PERIOD	GROUP 0	GROUP I	GROUP II	GROUP III	GROUP IV	GROUP V	GROUP VI	GROUP VII	GROUP VIII		
0		1 H 1.008									
I	2 He 4.00	3 Li 6.940	4 Be 9.020	5 B 9.020	6 C 12.000	7 N 14.008	8 O 16.000	9 F 19.000			
II	10 Ne 20.20	11 Na 22.997	12 Mg 24.32	13 Al 26.97	14 Si 28.06	15 P 31.027	16 S 32.064	17 Cl 35.46			
III	18 A 39.91	19 K 39.096	20 Ca 40.07	21 Sc 45.10	22 Ti 48.1	23 V 50.96	24 Cr 52.01	25 Mn 54.93	26 Fe 55.84	27 Co 58.94	28 Ni 58.69
		29 Cu 63.57	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.96	34 Se 79.2	35 Br 79.92			
IV	36 Kr 82.9	37 Rb 85.44	38 Sr 87 63	39 Y 88.9	40 Zr 91.0	41 Cb 93.1	42 Mo 96.0	43 Ma ?	44 Ru 101.7	45 Rh 102.91	46 Pd 106.7
		47 Ag 107.88	48 Cd 112.41	49 In 114.8	50 Sn 118.70	51 Sb 121.77	52 Te 127.5	53 I 126.93			
V	54 Xe 130.2	55 Cs 132.81	56 Ba 137.37	57-71 Rare Earths	72 Hf 180.8	73 Ta 181.5	74 W 184.0	75 Re 186.31	76 Os 190.8	77 Ir 193.1	78 Pt 195.23
		79 Au 197.2	80 Hg 200.61	81 Tl 204.39	82 Pb 207.20	83 Bi 209.0	84 Po 210.0	85 —			
VI	86 Rn 222.	87 —	88 Ra 225.95	89 Ac 227	90 Th 232.15	91 Pa 231.	92 U 238.17				

Periodic System Chart

Most of the above has been taken from Practical Chemistry Black and Conant The Macmillan Co , 1931, p 305 In the upper left hand corner of each rectangle is the atomic number while the

posed of a definite number of electrons and protons in fixed arrangement in relation to one another. The amount of electrons and protons will determine properties of the element, e.g., its activity. Some brilliant work has been done in this field by Louis, Langmuir, and Bohr. Their theories do not agree in every phase but the basic assumptions are the same. The atom consists of two parts: the nucleus which contains all the protons or positive charges and some of the electrons. It is rather compact and gives weight to the atom. The second part consists of one or more shells or orbits, surrounding the nucleus, which contain electrons. These electrons can revolve in a certain path around the nucleus. The number of electrons in the outer orbit may be 1–8 and all atoms containing the maximum number of electrons in the outer orbit are inert. Neon, which has 8 electrons on the outer shell, is a good example. Hydrogen contains a nucleus with one positive charge and one electron in the outer shell. Helium contains a nucleus with two positive charges and two electrons in the outer shell. The first shell is complete with two electrons, therefore, helium is an inert gas. The next element, lithium, contains a nucleus with three positive charges and two shells. The first shell contains two electrons and is complete. The next shell contains one electron. Beryllium likewise contains four positive charges in the nucleus and four negative charges in the two shells. The number of electrons increases until the second shell has 8 electrons and again the element having 8 electrons on the outer shell is inert, because the outer electron shell is complete. The next element has a third shell, etc.

With the electronic conception of the atom it is rather simple to explain the valence of an element. For instance, the hydrogen atom has one electron in the outer shell. Now, if this electron is taken away a hydrogen ion results because the positive charge of the nucleus is no longer neutralized. Thus, hydrogen loses

an electron in any of its reactions. Helium, the next in order, has the outer shell filled with two electrons. It cannot gain or lose electrons, so it is inert. Lithium has one electron in the outer shell, i.e., it can lose one electron and give a positively-charged ion, Li^+. Let us now consider the fluorine atom which has seven electrons in its outer shell. As stated before, this outer shell can contain a maximum of eight electrons. Now fluorine, in order to have this outer ring completed, can gain one electron or give up seven electrons. Ordinarily the gaining of one electron is easier for completing the outer shell. Therefore, hydrogen can combine with fluorine because hydrogen wants to give up one electron and become positive, while fluorine would like to absorb one electron and become negative. In this way, the compound HF (hydrogen fluoride) is readily formed. Thus, it may be said that the valence of a metallic element is the number of electrons which it will lose in becoming a positive ion. Similarly, the valence of a non-metallic element is the number of electrons which will be absorbed in order to complete the outer electron shell.

QUESTIONS

1. Sand, which is silicon dioxide, is sometimes occluded in iron castings. How would you remove this during the cleaning process?
2. Which iodides, bromides and chlorides are insoluble?
3. Describe the old periodic law. Describe the new periodic law.
4. Explain an inert atom.
5. What is the atomic number of an element?
6. What are the relative weights of the proton and the electron?
7. Give three cases where the elements are more correctly arranged according to Moseley's table than in the old Mendelejeff's table.
8. Give the advantages and disadvantages of Mendelejeff's periodic system.

9. How many grams of hydrogen chloride can be obtained by the combination of 10 grams of hydrogen with an excess of chlorine?
10. 22 cc of a 0.1 normal hydrochloric acid solution neutralizes 10 cc of an unknown sodium hydroxide solution. What is the normality of the NaOH?

CHAPTER X

The Phosphorus and Alkaline Earth Groups; Aluminum and Silicon

In the preceding chapter the halogen family was studied and then the periodic system and structure of matter was treated.

In this chapter, the phosphorus group, the alkaline earths, aluminum and silicon are discussed.

Nitrogen, phosphorus, arsenic, antimony and bismuth are members of the fifth group in the periodic system. Their place in the system indicates that they should have a valence of either three or five and these are common, except with bismuth, which practically has only a valence of three. With the decrease of the atomic weights, the members of this group display less and less metallic properties. Thus, antimony has many properties of a metal while bismuth is non-metallic. The halides of bismuth and antimony react with water to give insoluble oxyhalides.

Phosphorus is a very active element and, therefore, is never found in the uncombined state. It is found in nature as apatite, $3Ca_3(PO_4)_2.CaF_2$, which occurs in large deposits. Calcium phosphate occurs in the brains, tissues, bones, and muscles of animals. Many large deposits of calcium phosphate, $Ca_3(PO_4)_2$, are found in the United States and in North Africa. Phosphorus can best be obtained by heating a phosphate rock with

sand and coke in an electric furnace. The phosphorus distills off and is condensed and molded into sticks and then preserved under water. The reaction for this is:

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C = 6CaSiO_3 + 10CO + P_4$$

Phosphorus exists in two allotropical forms known as white phosphorus and red phosphorus. White phosphorus is a white, waxy, translucent solid which melts at 44°C and boils at 287°C. The molecule up to 1500°C is P_4. It is insoluble in water, but soluble in ether, carbon disulfide, turpentine, etc. It unites with oxygen at room temperature and, therefore, must be protected from the atmosphere. Red phosphorus can be formed by heating white phosphorus in the absence of oxygen up to 230 to 300°C. Red phosphorus is not soluble in solvents, is non-poisonous and will not take fire readily.

If phosphorus is burned in the air, dense white fumes appear which consist of phosphorus pentoxide.

$$4P + 5O_2 = 2P_2O_5$$

If this oxide is dissolved in boiling water, meta-phosphoric acid, HPO_3, is formed.

$$P_2O_5 + H_2O = 2HPO_3$$

Ortho-phosphoric acid is formed according to the reaction:

$$P_2O_5 + 3H_2O = 2H_3PO_4$$

This compound can be produced cheaply in commercial grade by allowing phosphate rock to react with sulfuric acid:

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$$

Phosphoric acid is used for preparing fertilizers, clarifyi sugar, treating metals, rustproofing, plating metals, and fi proofing.

Pyrophosphoric acid is prepared by burning ortho-phospho acid at 213°C.

$$2H_3PO_4 = H_2O + H_4P_2O_7$$

Meta-phosphoric acid can be made by heating ortho-phospho acid to 400°C.

$$H_3PO_4 = H_2O + HPO_3$$

From the formula, H_3PO_4 one would expect that met phosphoric acid forms three salts. There are three hydroge ions to be neutralized and, in this case, one, two, or three these can be displaced. Let us consider the case in which a three hydrogens are removed. If excess sodium hydroxide added to phosphoric acid, trisodium phosphate is formed, a cording to the equation below:

$$H_3PO_4 + 3NaOH = Na_3PO_4 + 3H_2O$$

Trisodium phosphate is used in large amounts for cleanin and rustproofing metals. If phosphoric acid is neutralized wit sodium hydroxide, using phenolphthalein as an indicator, diso dium phosphate is formed.

$$H_3PO_4 + 2NaOH = Na_2HPO_4 + 2H_2O$$

This substance is used in the silk industry and in the manu facture of phosphate plating baths, such as copper, platinum palladium, etc. The third salt, monosodium phosphate, is ob-

tained when molecular quantities of the two substances are mixed.

$$H_3PO_4 + NaOH = NaH_2PO_4 + H_2O$$

This phosphate is slightly acid when dissolved in water and is used in baking powders.

Arsenic is found in nature in the form of the sulfide, orpiment, As_2S_3, or arsenic pyrites, FeAsS. Free arsenic can be prepared from the oxide by heating with carbon.

$$2As_2O_3 + 3C = 4As + 3CO_2$$

Its physical properties resemble those of the metals but its chemical properties resemble those of the non-metals. The metallic arsenic is gray, brittle, and sublimes on heating. Arsenic is used commercially in alloy formation. Arsenous acid, H_3AsO_3, is formed by burning arsenic in oxygen and dissolving the oxide in water.

$$4As + 3O_2 = 2AS_2O_3$$
$$As_2O_3 + 3H_2O = 2H_3AsO_3$$

Arsenic acid, H_3AsO_4 is formed by the oxidation of the trioxide with nitric acid or chlorine water.

$$H_3AsO_3 + Cl_2 + H_2O = 2H_3Cl + H_3AsO_4$$

Trivalent arsenic reacts with hydrogen sulfide to precipitate the yellow arsenic trisulfide.

$$2AsCl_3 + 3H_2S = 6HCl + As_2S_3$$

Antimony can be found in the free state, but generally occurs

as stibnite in the form of Sb_2S_3. Free antimony can be prepared from stibnite by roasting with scrap iron.

$$Sb_2S_3 + 3Fe = 3FeS + 2Sb$$

In the periodic system, the change from the non-metallic elements to the metallic elements continues as the atomic weights increase and in arsenic some definite metallic properties are observed, and in antimony, the metallic properties are more pronounced. Antimony forms sulfates and chlorides with sulfuric and hydrochloric acids. Its hydroxides are acidic. Antimony itself is a poor conductor of heat and electricity, is silver-white and brittle. It melts at 630°C, boils at 1440°C and is used in making alloys.

Antimony sulfate is completely hydrolyzed, forming a very weak base. Antimony trichloride, also known as bitters of antimony, is used to give a dull finish to gun barrels. Antimony salts can be precipitated with hydrogen sulfide to form antimony trisulfide, which is an orange red precipitate.

$$2SbCl_3 + 3H_2S = 6HCl + Sb_2S_3$$

Bismuth occurs in the free state and also as the oxide and sulfide. It can be prepared from anode slimes in copper and lead tanks in electrolytic refining plants. It is usually made by reducing the sulfides with carbon or by electrolytic methods. It is a silver-white, partly crystalline metal. It melts at 269°C and boils at 1400°C. Bismuth nitrate is hydrolyzed very easily. It is used in making X-ray pictures of the intestines. If heated strongly metallic bismuth will burn to form the trioxide, Bi_2O_3.

Magnesium and calcium occur in group two of the periodic

table. There are two other members in this group, strontium and barium. They are also known as the alkaline earths. Radium also belongs to this group, but it is rare and is seldom considered when alkaline earths are discussed. Magnesium is common, but the metal is expensive due to the high cost of preparation. It occurs as magnesite, $MgCO_3$, and dolomite, $MgCO_3CaCO_2$ and aiso as $KClMgCl_2 \cdot 6H_2O$. Soapstone and asbestos are magnesium compounds, the first having the formula $MgH_2(SiO_3)_4$ and the latter $CaMg_3(SiO_3)_4$.

Magnesium is prepared by the electrolysis of fused magnesium chloride containing some sodium and potassium chlorides to lower the melting point of the mass. Magnesium is a silvery white metal which melts at 651°C and boils at 1000°C. It is very light, even lighter than aluminum. It is used in the manufacture of light alloys which have various uses in the industry, especially in the aviation field. Magnesium is a rather active metal and burns with a brilliant white light. Therefore, it is used for flashlight powders.

The white oxide of magnesium is obtained by heating magnesium carbonate.

$$MgCO_3 = MgO + CO_2$$

The hydroxide is insoluble in water and is used for medicinal purposes being known as milk of magnesia. This can be formed by boiling magnesium with water:

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$$

It can also be produced by precipitating any soluble magnesium salt with a hydroxide. For instance:

$$MgCl_2 + 2NaOH = Mg(OH)_2 + 2NaCl$$

Magnesium carbonate, $MgCO_3$, is mined in the United States and other countries. It is used in the manufacture of magnesium oxide and for lining open-hearth furnaces. Magnesium sulfate is mined in Germany and in the western part of the United States. If crystallized with seven molecules of water, that is $MgSO_4 \cdot 7H_2O$, it is known as epsom salt.

If a magnesium salt, such as magnesium chloride, is added to a solution of an ortho-phosphate in the presence of ammonium hydroxide, magnesium ammonium phosphate is precipitated.

$$Na_2HPO_4 + MgCl_2 + NH_4OH = 2NaCl + H_2O + MgNH_4PO_4$$

This compound, if heated, forms the pyro-phosphate, $Mg_2P_2O_7$, which is a very stable compound.

The compounds of calcium are very common constituents of the earth's crust. One of its most important salts is calcium carbonate, $CaCO_3$, which is found in the form of limestone or marble. The hydrated sulfate, gypsum, $CaSO_4 \cdot 2H_2O$, is also plentiful. Phosphorite, $Ca_3(PO_4)_2$, is found in the United States and Africa. The metal can be prepared by the electrolysis of the melted chloride. Calcium is a silver-white metal melting at 800°C. The hot metal is rather active, uniting with nitrogen and oxygen readily. It combines with hydrogen to form hydrolyte of the formula CaH_2. This will decompose when placed in water as follows:

$$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2$$

Calcium carbonate is practically insoluble in water but becomes more soluble if carbon dioxide is present.

$$CaCO_3 + H_2CO_3 = Ca(HCO_3)_2$$

When heated, it produces lime.

$$CaCO_3 = CaO + CO_2$$

Calcium carbonate will react with acids to produce carbon dioxide.

$$CaCO_3 + H_2SO_4 = CaSO_4 + H_2O + CO_2$$

Calcium carbonate can be prepared in the laboratory by adding any soluble carbonate to any soluble calcium salt.

$$K_2CO_3 + CaCl_2 = CaCO_3 + 2KCl$$

The calcium carbonate is precipitated as a finely divided powder and may be used as a polishing agent.

Quick lime is calcium oxide which is produced by heating calcium carbonate. It combines with water rapidly, liberating heat and forming calcium hydroxide. The reaction is called slacking and may be represented as follows:

$$CaO + H_2O = Ca(OH)_2$$

Calcium hydroxide, known as slacked lime, is slightly soluble in water. Its suspension in water is used to paint fences, barns, and the inside of plants when a cheap covering is desired. It may be used as an alkali provided concentrated solutions are not necessary. It also serves as a good wall paint in electroplating plants.

Calcium sulfate is generally mined as $CaSO_4 \cdot 2H_2O$. This mineral can be heated so that 75% of its water is driven off, leaving behind $CaSO_4 \cdot \frac{1}{2}H_2O$. Its formula may also be written as $2CaSO_4 \cdot H_2O$. It is known as plaster of Paris. When mixed

with a certain amount of water, it sets to a white hard solid in about 10 minutes. Plaster of Paris is used for making molds, for plastering walls, etc.

Calcium chloride is used for preventing the formation of dust on roads and in a refrigerating brine for ice plants.

Strontium occurs naturally as carbonate and sulfate. Strontium nitrate, if mixed with sulfur, charcoal, and potassium chlorate, produces fireworks which give off red flames.

Strontium hydroxide, $Sr(OH)_2$, is produced by heating the carbonate in the presence of steam.

$$SrCO_3 + H_2O = CO_2 + Sr(OH)_2$$

The chief mineral of barium is barite, $BaSO_4$, which is the raw material for the preparation of barium salts. If it is roasted with coal, barium sulfide, BaS, is produced. If sodium sulfate is added to the sulfide "Blanc fixe" results which is precipitated barium sulfate.

$$BaS + Na_2SO_4 = Na_2S + BaSO_4$$

"Blanc fixe" is a pure white pigment which is used in paints and inks. Barium nitrate is used to produce green lights in fireworks, etc.

Aluminum is plentiful in nature. Being quite active, it is not found in the free but always in the combined state. There are many compounds of aluminum such as felspar, $KAlSi_3O_8$, clay, which is known as kaolin, $(H_2Al_2)(SiO_4)_2 \cdot H_2O$, and mica, $KAlSiO_4$. There are many other compounds of this element including some precious stones. Cryolite and bauxite are industrially important from the standpoint of the manufacture of aluminum. The first mineral has the formula $3NaF \cdot AlF$, while the second is a hydrated oxide, $Al_2O_3 \cdot 2H_2O$.

C. M. Hall, in 1886, discovered that aluminum oxide could be electrolyzed if placed in a molten solution of cryolite. The apparatus consists of an iron container which is lined with carbon. The carbon acts as the cathode and the anode consists of sticks of carbon which are held in place by copper clamps. The cryolite is first melted by the current, then the bauxite is introduced and electrolysis starts. Aluminum, being heavier than the bath, sinks to the bottom of the cell and is withdrawn at proper intervals. Aluminum is a silver white metal which melts at 660°C. It tarnishes very slightly but in so doing forms an oxide coating which acts as a protective film on the surface of the metal. It is very light and is a good conductor of electricity and heat. Aluminum reacts vigorously with hydrochloric acid.

$$2Al + 6HCl = 2AlCl_3 + 3H_2$$

It also reacts with alkalies.

$$2Al + 6NaOH = 2Na_3AlO_3 + 3H_2$$

It has a very great affinity for oxygen, so that it will displace many other elements from their oxides. If ferric oxide is mixed with aluminum powder and ignited, the temperature is immediately raised above 3000°C. The aluminum displaces the iron which remains in the molten state. The iron will take the shape of the container and is used for welding pieces of iron and steel together. This process is called aluminothermy. The reaction is as follows:

$$Fe_2O_3 + 2Al = Al_2O_3 + 2Fe$$

Aluminum oxide is found as bauxite which is partially hydrated aluminum oxide. Al_2O_3 is very hard and can be used

for abrasives or polishing materials. It is made by fusing bauxite with coke. Ruby and sapphire gems consist of native aluminum oxide which has been colored by other metallic oxides, being present in very small amounts.

Aluminum hydroxide, $Al(OH)_3$, is formed when any soluble aluminum salt is treated with a soluble base.

$$6NH_4OH + Al_2(SO_4)_3 = 2Al(OH)_3 + 3(NH_4)_2SO_4$$

The aluminum hydroxide formed can be dissolved with any acid as it is a base.

$$Al(OH)_3 + 3HCl = AlCl_3 + 3H_2O$$

Aluminum hydroxide has not only basic but also acid properties. It reacts with sodium or potassium hydroxide.

$$Al(OH)_3 + 3KOH = K_3AlO_3 + 3H_2O$$

If a substance acts as either a base or as an acid it is said to be amphoteric. Aluminum hydroxide reacts as either an acid or a base, i.e., ionizes in two different ways: It gives rise to hydrogen or hydroxyl products. As an acid, aluminum ionizes as follows:

$$H_3AlO_3 = 3H^+ + AlO_3^{---}$$

and as a base, it ionizes as follows:

$$H_3AlO_3 = Al^{+++} + 3OH^-$$

When aluminum hydroxide acts as an acid it is called aluminic acid and its salts are called aluminates.

Aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$, is prepared by treat-

ing clay or kaolin with sulfuric acid. The insoluble silicic acid is removed by filtration.

$$H_2Al_2(SiO_4)_2 + 3H_2SO_4 = Al_2(SO_4)_3 + 2H_4SiO_4$$

The aluminum sulfate can be obtained by crystallization.

All alums consist of an electropositive ion having a valence of one united with the sulfate radical in combination with a positive ion having a valence of three united with the sulfate radical and the whole containing twenty-four molecules of water of crystallization. An example is sodium aluminum sulfate, $Na_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$. It is not absolutely essential for an alum to contain aluminum. It can contain any trivalent atom instead.

Silicon can be produced by the reduction of sand with magnesium powder.

$$2Mg + SiO_2 = Si + 2MgO$$

It can also be prepared by heating sand with coke in an electric furnace:

$$2C + SiO_2 = 2CO + Si$$

The most important compound of silicon is silicon dioxide or silica, SiO_2. One of its purest forms is quartz and ordinary sand is another less pure form. Hydrofluoric acid acts upon silicon dioxide as follows:

$$SiO_2 + 4HF = 2H_2O + SiF_4$$

Sand is used in glass manufacture. Silicon dioxide has a very high melting point and a small coefficient of expansion. For this reason, it can be heated to red heat and dropped into water

without cracking. Silica also transmits ultra-violet rays which is of use in medicine for ultra-violet treatments. If silicon dioxide is boiled with sodium hydroxide it forms sodium metasilicate, Na_2SiO_3.

$$SiO_2 + 2NaOH = Na_2SiO_3 + H_2O$$

This also may be made by fusing with potassium carbonate.

$$SiO_2 + K_2CO_3 = K_2SiO_3 + CO_2$$

If sodium and potassium carbonates are fused with a large quantity of sand, glass is produced, according to the following equation:

$$SiO_2 + CaCO_3 = CO_2 + CaSiO_3$$

This substance becomes viscous on cooling and then solidifies. However, it does not crystallize, but stays in the amorphous state.

If coke and sand are heated in an electric furnace, an exceedingly hard substance is produced that is called silicon carbide. The reaction is as follows:

$$3C + SiO_2 = SiC + 2CO$$

The crystals resulting are purple in color and can be used, when pulverized, for grinding wheels, grinding compounds, etc.

QUESTIONS

1. Name and give the formula for the three acids of phosphorus.
2. What is bitters of antimony?
3. Name the members of the phosphorus family.

4. Give the reaction for the slacking of lime.
5. Would you expect aluminum chloride to be acid or basic when dissolved in water?
6. Write the equation for the anodization of aluminum.
7. Calculate the percentage composition of Al_2O_3.
8. How much quick lime can be obtained from 1000 pounds of limestone which is 95% pure calcium carbonate?

CHAPTER XI

Iron, Cobalt and Nickel; Zinc, Cadmium and Mercury; Tin and Lead

In the previous chapter the phosphorus group and the alkaline earths, aluminum and silicon were studied. In this chapter iron and cobalt and nickel are discussed. We shall also get acquainted with the group of zinc, cadmium and mercury, and the group of tin and lead.

Iron, cobalt, and nickel do not compose necessarily a group, but are transition elements, which lie between the first and second octaves of the periodic system. Iron resembles chromium and manganese in some respects, whereas nickel is somewhat similar to copper and zinc. All the metals of this family are magnetic, their decreasing order being as follows: iron first, cobalt second, and nickel last. Iron is the most important member of this group.

Iron ores of the greatest importance are the oxides: haematite, Fe_2O_3, and magnetite, Fe_3O_4. The carbonate, siderite, $FeCO_3$, is also used. Pyrites, FeS_2, is used on account of its sulfur content in the manufacture of sulfuric acid. This mineral, because of its golden-yellow, shining cubes, is known as fool's gold.

Iron is obtained from the oxides with the aid of a reducing agent. Generally, coke is used for this purpose. The coke burns to form carbon monoxide and this, in turn, reduces the iron.

$$2C + O_2 = 2CO$$

$$Fe_2O_3 + 3CO = 2Fe + 3CO$$

The equipment used to reduce iron ore is known as a blast furnace, and is generally 50–100 feet high, cylindrical in shape, constructed with steel and lined with fire brick. Inlets at the bottom of the furnace deliver hot compressed air to the stack. The ore, coke, and the materials which will form a fusible slag, such as limestone, are introduced at the top of the furnace. The reduction takes place, as the temperature increases, through combustion of the coke. In the bottom, melted iron and slag will form in two layers. The slag, being much lighter than the iron, floats on top and is withdrawn at definite intervals. The iron in the molten state is withdrawn from the lower tap. Carbon monoxide is formed, as indicated before. The iron produced in this furnace contains many impurities such as silica, sulfur, phosphorus, and carbon, and is known as pig iron. It contains about 94% iron, with about 2.5–4.3% carbon, also silicon, manganese, phosphorus and sulfur. Pig iron is used in making castings, stoves, pipes, radiators, furnace grates, etc. One of its unique properties is that, on becoming solid, it expands and therefore fills every part of a mold, which is ideal for casting. It can be obtained in two forms. Cementite, Fe_3C, is a very hard and very brittle product, which is obtained by chilling the iron quickly. It is rather white as compared with the other type which is known as gray cast iron. This is much softer than cementite; it contains iron in the pure state, and carbon in the form of graphite.

Wrought iron is made by heating pig iron which is placed upon a layer of iron oxide and hammer slag (basic silicate of iron). The heating takes place in a reverbatory furnace. The flame and heat are generated in one compartment and deflected

by the low roof on the material to be heated. The phosphorus, silicon, and carbon, present as impurities in the iron, combine with the oxygen of the oxide and dissolve in the slag present. The sulfur unites with the iron to form ferrous sulfide and also passes into the slag. As the iron becomes free from impurities, it passes from the liquid into an almost semi-solid state. This operation produces a very good grade of iron, being around 99.85% pure, but the process is expensive. The Bessemer and open-hearth products have displaced this type of iron.

Steel contains carbon in different amounts but is free from phosphorus, silicon, and sulfur. The amount of carbon will depend upon the use of the material. Structural steel contains around 0.4% carbon, while tool steel contains up to 1.5%. Steel can be magnetized, tempered and has a high tensile strength.

Much steel is made by the Bessemer process. This consists of pouring the molten cast iron into an egg-shaped converter which is made of steel and lined with sand and clay; it has openings at the bottom which permit the passage of air into the melt. The oxidation of some iron and the impurities, which are manganese, silicon, and carbon, generates a high temperature. When the reaction is complete, the desired amount of carbon is added and the steel discharged.

Many times, Bessemer steel is not desirable as it contains phosphorus. This may be removed in an open-hearth furnace which contains a wide, shallow bed with a low roof. The lining is composed of lime and magnesia for the basic and sand for the acid process. The fuel used is generally gas. The gas and air are both preheated before entering the furnace proper. This process will remove carbon, sulfur, silicon, and also phosphorus. The steel produced is used for rails and other high-grade products.

Steels, particularly alloy steels, are also produced in electric furnace, which permits a more careful adjustment of conditions in the manufacture of steel products than either the open-hearth or the Bessemer furnace. Oxidation or reduction can be carried to any point desired. Sulfur and phosphorus can be eliminated until only traces remain. As a general rule, higher temperatures, closer control, and better working conditions are obtained with an electric furnace, but the cost is higher than with the other types.

For special purposes, a very poor open-hearth steel is remelted with charcoal or pig iron in clay, graphite or clay crucibles. This is known as crucible steel and is employed in making dies, cutlery and razors.

If steel is heated above 900°C the carbon unites chemically with the iron to form cementite, Fe_3C. If cooled very quickly, the cementite does not have a chance to be precipitated out of solution but remains in the steel, making it quite hard. However, if the iron is cooled slowly, cementite crystals separate at around 700°C and produce a softer and tougher iron. This is known as tempering. By first chilling a piece of iron and then heating it up and cooling slowly, many variations of tempering can be obtained.

There are many alloys of steel, which are many times stronger and are more resistant to corrosion than steel alone. Steel, with 2–4% nickel, resists corrosion and is very hard. With 36% nickel the alloy is called invar and is practically non-expansive when heated. Invar is used for pendulum rods, etc. Duriron contains about 15% silicon, is insoluble in sulfuric, nitric, or acetic acid, and is used in the chemical industry for acid containers. Manganese steel contains 12–14% manganese, is a very hard alloy, and does not lose its temper when heated by friction. It is used for the jaws of rock-crushing machinery.

Chromium-vanadium steel, which contains 1% chromium and 0.15% vanadium, has great tensile strength, and is used for axles and connecting rods on automobiles.

Tungsten steel contains 8–20% tungsten and 3–5% chromium, and is used for high-speed tools as it can become red hot by friction without losing its temper.

Case-hardened steel is prepared by heating in contact with powdered carbon. The carbon unites with the surface iron to produce a hard steel layer over a body of softer material. Therefore, this steel has a hard exterior and a soft, tough interior.

Nitrided steel is similar to case-hardened steel except that nitrogen is the hardening agent. The hot metal absorbs the nitrogen from ammonia and other nitrogen compounds and forms iron nitrides on the surface. This yields a material which has a very hard surface and a soft interior.

Stainless steel, an alloy containing 18% chromium, 8% nickel, and 0.2% carbon, has remarkable corrosion-resisting properties. It is known under various trade marks. The general name for the alloy is stainless steel.

There are many iron compounds. Iron with a valence of two produces ferrous compounds. Ferrous sulfide, FeS, can be prepared by heating iron and sulfur together. It reacts with acids producing H_2S—a valuable laboratory reagent which is used by the chemist in analyzing compounds.

$$2HCl + FeS = FeCl_2 + H_2S$$

Ferrous sulfate is obtained by oxidizing pyrites in the air and leeching the resulting material.

$$2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4$$

Iron compounds containing trivalent iron are known as ferric compounds. Ferric hydroxide is a brown, gelatinous substance, insoluble in water and can be made by adding a base to a solution of a ferric salt. Thus:

$$FeCl_3 + 3NaOH = Fe(OH)_3 + 3NaCl$$

Ferric oxide is used as a red pigment. It is obtained from ferrous sulfate. The solution is allowed to oxidize and the ferric hydroxide is precipitated by adding lime. The precipitate is then calcined. It is also found in natural deposits.

Ferric sulfate, $Fe_2(SO_4)_3$, is formed by the oxidation of ferrous sulfate.

Potassium ferrocyanide, $K_4Fe(CN)_6$, ionizes as follows:

$$K_4Fe(CN)_6 \rightleftharpoons 4K^+ + Fe(CN)_6^{----}$$

If a ferric salt is added to an aqueous solution of the above, a deep blue precipitate results which is ferric ferrocyanide, also known as Prussian blue.

$$4FeCl_3 + 3K_4Fe(CN)_6 \rightarrow Fe_4[Fe(CN)_6]_3 + 12KCl$$

If chlorine is passed through a solution of potassium ferrocyanide, potassium ferricyanide is formed.

$$2K_4Fe(CN)_6 + Cl_2 \rightarrow 2K_3Fe(CN)_6 + 2KCl$$

Potassium ferricyanide unites with ferrous salts to form a deep blue precipitate known as Turnbull's blue which is ferrous ferricyanide.

$$3FeCl_2 + 2K_3Fe(CN)_6 \rightarrow Fe[Fe(CN)_6]_2 + 6KCl$$

Cobalt occurs as an arsenide along with nickel. Its two chief ores are smaltite, $CoAs_2$, and cobaltite, CoAsS. It is a silver-white metal with a faint trace of blue coloring. It is used in making alloys and in electroplating. Cobalt forms cobaltous (Co^{++}) and cobaltic compounds (Co^{+++}).

Cobaltous chloride, $CoCl_2 \cdot 6H_2O$, is made by treating the oxide with hydrochloric acid. It forms red crystals, but if dehydrated its color becomes deep blue. Cobalt sulfide, CoS, a black substance, is precipitated from the solution of any of its soluble salts by the addition of ammonium sulfide.

Cobaltic hydroxide, $Co(OH)_3$, a black powder, is precipitated by adding a hypochlorite to a cobaltous salt solution. If the nitrate is heated carefully, a cobaltic oxide, Co_2O_3, is formed. Cobalt is similar to iron in that it has a valence of two or three.

Nickel occurs as niccolite, NiAs, and nickel glance, NiAsS. The Canadian ores supply about 90% of the world's demand. The ores are roasted and treated by the Bessemer process which produces a matte. This is "blown" until all the iron is removed, which leaves behind the sulfides of nickel and copper. These are then reduced to the metals. The alloy produced is separated by an electrolytic process. Nickel is a white magnetic metal which has many properties similar to those of iron. It melts at 1452°C and is used in making alloys, in nickel plating and as a catalyst in many chemical reactions.

There are two series of nickel compounds, nickelous and nickelic compounds. Nickelous hydroxide, $Ni(OH)_2$, is formed when a base is added to any soluble nickelous salt. If this is heated, green nickelous oxide, NiO, results. Nickelic hydroxide, $Ni(OH)_3$, a black precipitate, is formed when a hypochlorite is added to a salt of nickel. Nickelous sulfide, NiS, can be precipitated by adding ammonium sulfide to a soluble nickel salt. It is similar to cobaltous sulfide. The addition of dimethyl-

glyoxime to an ammoniacal solution of nickel salt produces an insoluble red precipitate:

$$NiCl_2 + (HON)_2C_2(CH_3)_2 = 2HCl + NiH_6C_4O_2N_2$$

We shall discuss now zinc, cadmium and mercury, which are in group II of the periodic system, and also tin and lead which are in group IV. These metals are used in every-day life and for the manufacture of mechanical devices. The first metal to be studied is zinc. It is found in various parts of the United States, but the largest fields are in Missouri, Kansas, and Arkansas. The ore is a mixture of lead and zinc sulfide. The zinc sulfide ore is known as sphalerite. This ore is first concentrated, which consists of separating the zinc sulfide from the gangue. This is generally done by flotation process and the resulting ore can be treated in a number of ways in order to produce the metal. Pyrometallurgy can be used, i.e., the sulfide can be reduced to the oxide by roasting, and the oxide is then reduced with carbon. The reactions are as follows:

$$2ZnS + 3O_2 = 2ZnO + 2SO_2$$

$$ZnO + C = Zn + CO$$

The metal can be obtained by melting the product and casting into slabs. The temperature necessary for the reduction to take place is 1200°C. As the boiling point of zinc is 907°C, all metal produced by this method is in the vapor state and must be condensed in the proper apparatus. If the temperature of the container is above 420°C liquid zinc is obtained which can be withdrawn and poured into slabs.

Another process for preparing zinc is the electrolytic method. This consists in first roasting the sulfide ore with air:

$$ZnS + 2O_2 = ZnSO_4$$

The zinc sulfate thus produced is dissolved out by using sulfuric acid solution. As there are also other metals in this solution, zinc dust is added to precipitate any metals less active than zinc. The solution thus produced is a rather pure solution of zinc and is run into electrolytic cells using lead as the anode and aluminum as the cathode. A current density of 30–100 ampères per square foot is applied. A very pure zinc is obtained at the cathode. This method is gaining rapidly in commercial practice and is now used for producing many other metals besides zinc.

Zinc is a silvery-white metal which is rather brittle at ordinary temperatures. However, if heated to 100–150°C, it can be rolled into thin sheets. The melting point is around 410°C. It corrodes slowly in the air, forming a basic carbonate on the surface. This coating acts as a protector for the metal and prevents excessive corrosion. However, by the formation of this coating, the metal will tarnish very quickly. It will displace hydrogen from acids.

$$2HCl + Zn = ZnCl_2 + H_2$$

It will also displace hydrogen from steam if the metal is hot.

$$Zn + H_2O = ZnO + H_2$$

One of the most important uses of zinc is in covering iron surfaces for protection against corrosion. The zinc is applied by three different methods: galvanizing, sherardizing, and electrogalvanizing. The iron, in all cases, is first cleaned by dipping into sulfuric acid or other suitable liquid so that the oxide surface is dissolved. In galvanizing, the iron is dipped into a molten zinc bath, for applying a thin coating of zinc

to the surface of the iron. In the sherardizing method, after the iron has been cleaned, it is covered with zinc dust and the temperature raised until the zinc is fused to the surface. Electrogalvanizing consists of making the iron the cathode in electrolytic zinc solution and passing a current through, thereby depositing zinc on the iron. Zinc is used also in making alloys, one of the best known being brass, which is a mixture of copper and zinc. It is used in the manufacture of zinc oxide for the paint industry. Zinc is soluble in hot alkali producing zincates.

$$2NaOH + Zn = Na_2ZnO_2 + H_2$$

Zinc sulfate, $ZnSO_4$, is called white vitriol and is used in preserving hides and as a mordant in cotton printing. It is also used in the electroplating of zinc, etc.

Zinc sulfide, ZnS, is the only white sulfide of the metals, therefore, it is used as an ingredient of a white pigment known as lithopone. This consists of a mixture of barium sulfate and zinc sulfide, which is prepared by the action of barium sulfide on zinc sulfate.

$$BaS + ZnSO_4 = BaSO_4 + ZnS$$

The substances produced in this reaction are insoluble and the mixture has greater covering power than white lead, does not darken when exposed to hydrogen sulfide and is non-poisonous.

Zinc chloride, $ZnCl_2$, is generally manufactured by allowing hydrochloric acid to react with the metal. The salt thus formed can be crystallized from the solution provided an excess of hydrochloric acid is present. The aqueous zinc chloride solutions are used for cleaning metals before soldering.

Zinc oxide, a white powder, is obtained by burning the metal.

$$2Zn + O_2 = 2ZnO$$

It is used in making paints and as a filler in automobile tires.

Zinc hydroxide, $Zn(OH)_2$, is a white, flocculent, insoluble substance produced by adding a base to a soluble zinc salt.

$$ZnSO_4 + 2NaOH = Zn(OH)_2 + Na_2SO_4$$

Zinc hydroxide is soluble in excess of base.

$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O$$

One can see that zinc hydroxide acts as a weak acid or a weak base. Compounds that contain the ZnO_2 radical are called zincates. Thus, Na_2ZnO_2 is called sodium zincate. Zinc combines with the cyanide radical to produce zinc cyanide, $Zn(CN)_2$, and this compound will combine with alkali cyanides to form complex double cyanides.

$$Zn(CN)_2 + 2NaCN = Na_2Zn(CN)_4$$

Zinc cyanide also reacts with sodium hydroxide:

$$2Zn(CN)_2 + 4NaOH = Na_2Zn(CN)_4 + Na_2ZnO_2 + 2H_2O$$

This reaction is important because most of our zinc plating cyanide baths are made up in this manner. This solution gives a very good deposit of zinc if electrolyzed.

There are no important minerals of cadimum. Cadmium ores occur along with zinc ores. Cadmium is always a by-product

of the zinc industry. The metal is obtained from the zinc solution, as has been pointed out before, by introducing some zinc dust into the solution and zinc displaces the cadmium and other metals which fall to the bottom as a precipitate. The cadmium is then dissolved as the sulfate and electrolyzed. The resulting pure cadmium is a white metal which melts at 321°C and is much more malleable than zinc. It is used in making low-melting-point alloys for electroplating and as an alloy constituent for bearings. Copper and cadmium form a very good bearing material which is now used to a great extent in the automobile field.

Cadmium chloride crystallizes as $CdCl_2 \cdot 2H_2O$. The white floculent hydroxide is precipitated by the reaction of a soluble cadmium salt with a base.

$$CdCl_2 + 2NaOH = Cd(OH)_2 + 2NaCl$$

Cadmium hydroxide is not soluble in excess base, i.e., it is not amphoteric. However, cadmium hydroxide will dissolve in ammonium hydroxide, forming cadmium ammonium hydroxide, $Cd(NH_3)_2(OH)_4$.

Cadmium sulfide, CdS, is produced by adding H_2S to a soluble cadmium salt. Its color is yellow to red.

$$CdCl_2 + H_2S = CdS + 2HCl$$

Cadmium sulfide is used as a pigment in paints, etc.

Cadmium cyanide or cadmium oxide reacts with alkali cyanides to form double cyanides, $NaCd(CN)_3$.

Mercury is a silvery-white liquid which becomes solid at −38.9°C and boils at 357°C. It is used in barometers and thermometers, and in forming amalgams with other metals. Mercury sometimes occurs in the native state, but more often

as mercuric sulfide, HgS, which is called cinnabar. When roasted, the sulfide is decomposed as follows:

$$HgS + O_2 = Hg + SO_2$$

Mercury does not displace hydrogen from dilute acids but will react with oxidizing acids, for example, nitric acid, yielding the corresponding nitrates. Mercury is monovalent or divalent. Mercurous salts contain monovalent mercury, whereas mercuric salts are the compounds of divalent mercury.

Mercurous chloride, HgCl (calomel), is used for medicinal purposes and is made by heating mercuric chloride with mercury.

$$HgCl_2 + Hg = 2HgCl$$

Mercuric chloride can be formed by combining chlorine with mercury.

$$Hg + Cl_2 = HgCl_2$$

This salt, known as bichloride of mercury, is very poisonous, and if taken internally causes death. Note the great difference in the physiological action of the two compounds.

Mercuric oxide, HgO, is a red crystalline powder formed when mercury is heated in the arc to 360°C.

Mercurous oxide, Hg_2O, is formed if sodium hydroxide is added to solutions of mercurous salts. Mercuric nitrate, $Hg(NO_3)_2$, is produced by allowing warm, concentrated nitric acid to react with mercury. Mercury blue dips are made by adding one ounce of mercuric chloride, $HgCl_2$, per gallon of the bath and one half ounce of ammonium chloride per gallon. This solution is often used to cover iron, steel, or brass with a thin layer of mercury so that silver or other metals are not

deposited by immersion when placed in an electrolytic bath. The reaction occurring when iron is put into this dip is as follows:

$$HgCl_2 + Fe^o = FeCl_2 + Hg^o$$

The resulting mercury adheres tenaciously and covers all parts of the exposed iron.

The most important ore of tin is cassiterite or tin stone, which is the dioxide, SnO_2. This is mined in Bolivia and the East Indies. Cassiterite is concentrated by washing so that all foreign material is removed. It is then roasted to remove sulfur and arsenic. Next, carbon is added in one form or another and the oxide is reduced.

$$SnO_2 + C = Sn + CO_2$$

The metal is generally purified by heating gently on a sloping hearth. The melting point of tin being much lower than that of its impurities, tin melts and flows away from them. The molten metal is then collected in molds as block tin. The metal exists in three solid forms, each having a definite transition temperature. Below 18°C, a gray modification is the stable form. This tin is very brittle and crumbles to powder. At ordinary temperatures, tin is a white, crystalline metal, having little tensile strength but being very malleable. Tin is used for the manufacture of tinplate which consists of iron covered with tin. It is also used in the manufacture of tinfoil and in the preparation of alloys, such as Brittania, bronze, Babbitt, and type metal.

Tin has a valence of two or four. The first compounds are known as stannous, while the second compounds as stannic.

Tin displaces hydrogen from acids.

$$Sn + 2HCl = H_2 + SnCl_2$$

It unites with nitric acid in a special manner, forming stannic compounds instead of the stannous compounds.

$$3Sn + 4HNO_3 + H_2O = 3H_2SnO_3 + 4NO$$

Tin also reacts with sodium hydroxide forming sodium stannite.

$$Sn + 2NaOH = H_2 + Na_2SnO_2$$

Stannous chloride, $SnCl_2 \cdot 2H_2O$, is made by the interaction of hydrochloric acid with tin. Stannous chloride will change to stannic chloride, $SnCl_4$, rather easily and thus, it is an active reducing agent. It will reduce ferric salts to ferrous salts.

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$$

Stannous chloride reacts with sodium hydroxide to produce stannous hydroxide, $Sn(OH)_2$.

$$2NaOH + SnCl_2 = Sn(OH)_2 + 2NaCl$$

This hydroxide is similar to zinc and aluminum hydroxide in that it is soluble in both strong acids and strong bases. Therefore, it is amphoteric.

Stannous sulfide, SnS, is insoluble in water and has a brown black color. It is produced as follows:

$$SnCl_2 + H_2S = SnS + 2HCl$$

It unites with sulfides to form sulfostannates.

$$SnS + Na_2S_2 = Na_2SnS_3$$

Stannic chloride, $SnCl_4$, is produced when chlorine acts upon tin or upon stannous chloride.

$$2Cl_2 + Sn = SnCl_4$$

If ammonium hydroxide is added to $SnCl_4$ the following reaction takes place:

$$SnCl_4 + 4NH_4OH = 4NH_4Cl + H_2SnO_3 + H_2O$$

H_2SnO_3 is called stannic acid. It decomposes very easily into the oxide and water.

$$H_2SnO_3 = H_2O + SnO_2$$

Galena, PbS, lead sulfide, is the most important ore of lead, another ore being cerussite, $PbCO_3$. Lead is obtained by roasting the ore to convert it into oxide. It is then mixed with coke and limestone and reduced. The result is metallic lead and a slag that forms at the bottom of the furnace and can be easily separated. The lead thus obtained is rather impure and has to be separated from antimony, arsenic, bismuth, and copper. This can be done by melting the lead and stirring. The impurities which are oxides, float to the surface and can be removed. Gold and silver are present many times and these, along with the other impurities, can be removed by an electrolytic process. This consists of making the impure lead slabs the anode in a bath of hydrofluosilicic acid and lead silicofluoride. A small amount of gelatin is present as an addition agent to give a smooth deposit. The impurities drop to the bottom of the tank and the pure lead deposits at the cathode.

Lead is a heavy, soft, white metal melting at 307°C and boiling at 1525°C. It is mono-, di-, tri- or tetravalent. The metal easily oxidizes, forming the oxide and basic carbonate.

There are five oxides, Pb_2O, lead suboxide, gray; PbO, lead monoxide or litharge, yellowish-red; Pb_2O_3, lead trioxide, orange yellow; PbO_2, lead dioxide or peroxide, chocolate brown; Pb_3O_4, lead tetroxide, minium or red lead, red. PbO is formed by heating lead in the air above 600°C. Pb_3O_4 is obtained by heating PbO under 545°C.

Lead sulfate is produced by the combination of sulfuric acid or any sulfate with a lead salt. It is insoluble in sulfuric acid and for that reason a protective coating is formed on lead when it is introduced into a sulfate. Thus, we say that lead is insoluble in sulfuric acid, which, in reality, is not true. Lead is soluble in the acid, but insoluble lead sulfate forms on the surface and stops all reaction by insulating the lead from the solution.

It has been mentioned that different metals have different activity, thus, iron will displace tin from solution and zinc will displace iron. Zinc will also displace cadmium or copper from solution. The metals can be arranged according to their activity. For instance, the most active can be placed at the top of the list and the least active at the bottom. Thus the following order is obtained:

Potassium
Sodium
Calcium
Magnesium
Aluminum
Zinc
Chromium
Iron
Cadmium
Cobalt
Nickel
Tin
Lead

Hydrogen
Antimony
Arsenic
Bismuth
Copper
Mercury
Silver
Platinum
Gold

This list simply means that near the top the elements are very active. For instance, potassium and sodium react very quickly with water. Calcium also reacts with water, but not as rapidly. Coming down the list the activity is decreased and it is found that magnesium, aluminum, zinc, and iron will not react very quickly with water, but will readily react with dilute acids. At the bottom of the column is gold, the least active metal which is insoluble in all acids except aqua regia (a mixture of nitric and hydrochloric acids). If gold is in solution and some metallic platinum is added to this solution, the platinum will dissolve and the gold separates. Silver, being higher in the series, will displace platinum or gold from its solution. Mercury will displace silver, platinum or gold. The metal above will displace all metals below, thus potassium is the most active metal and will displace all others from their solution.

By using the electromotive series, it is possible to produce power. When one metal displaces another from solution, there is a transfer of electrons. Thus when zinc displaces copper from solution, the following occurs:

$$Zn^{o} + Cu^{++} = Cu^{o} + Zn^{++}$$

The zinc has given up two electrons to the copper. These electrons, when flowing, produce power and, of course, work can be done by utilizing this power. Thus, if a stick of zinc is placed

in a solution of copper sulfate, copper is deposited on the zinc rod. In this case the zinc becomes the anode and the copper becomes the cathode of the battery. This can further be illustrated by introducing a stick of copper and zinc into a dilute solution of sulfuric acid. If the two metals are now connected by a wire, a current will flow between them. Upon analyzing the solution, it will be found that zinc sulfate is present. In this case, also, the zinc is the anode and dissolves in the solution while the copper is the cathode. Thus, chemical energy is converted into electrical energy.

Corrosion may be explained on the basis of several theories, but the best seems to be the electrochemical theory. This is based on the electromotive series. Every metal or alloy has a definite tendency to go into solution and form ions. The higher in the series, the more the metal will have a tendency to form ions. Also, the higher metals will displace the lower metallic ions from solution. Taking iron in contact with moisture as an example, the following will often happen:

$$Fe + 2H^{+} \rightleftharpoons Fe^{++} + 2H$$

It will be noted that hydrogen acts like a metal and is displaced from solution by iron.

In order that the above equation should go to the right, the liberated hydrogen has to be removed. Otherwise, it will act as an insulator and stop all corrosion. The hydrogen can be removed in two ways:

$$(1)\ 4H + O_2 = 2H_2O$$
$$(2)\ 2H = H_2$$

In the first case, free oxygen, which is present dissolved in most natural waters, unites with the atomic hydrogen to produce water. In the second case, the atomic hydrogen combines

to form molecular hydrogen which is liberated as a gas. The higher the concentration of the hydrogen ions, the easier it is to corrode the metal. However, it must be borne in mind that the hydrogen film must be removed, so that the rate of reaction will be determined by the velocity of reactions (1) and (2).

It will be seen that the iron displaces hydrogen. Therefore, the surface where the iron dissolves becomes the anode, while the area on which the hydrogen is deposited becomes the cathode. Thus, iron is oxidized while hydrogen is reduced.

It is possible to have anodic and cathodic areas on the same piece of metal. This is often true with a piece of steel. A strain or bend in any part of a piece of steel will make that area anodic and the unchanged area will be the cathode. Impurities in the metal also give rise to anodic areas. Dissimilar pieces will very definitely bring about corrosion. For example, steel and stainless steel should never be used together under moist conditions, unless the steel is protected. The steel becomes the anode and dissolves, whereas the stainless steel becomes the cathode and is not injured.

It is possible to stop corrosion by stopping the above reaction. This may be done by applying protective coatings, removing moisture, etc. The prevention of corrosion is a study within itself and is only touched here.

QUESTIONS

1. What determines the physical properties of steel besides its chemical composition?
2. What properties of cobalt and nickel are similar to those of iron?
3. How would you distinguish between nickel and cobalt salts?
4. Name two reducing agents used in metallurgy.
5. What is the use of zinc chloride for soldering?

6. What is the electromotive series?
7. Which is the better coating for steel: tin or zinc?
8. Why are zinc compounds used in the paint industry?
9. How much coke, 95% carbon, would be needed to reduce one ton of PbS?
10. Give a use for mercury in the plating industry.

CHAPTER XII

Copper, Silver, Gold, Platinum, Rhodium, Tungsten, Chromium, Molybdenum and Vanadium

In the last section, some metals were discussed. In this chapter, the metals which are of primary importance to the electroplater are discussed and others are generally mentioned. Copper, silver, gold, platinum, rhodium, tungsten, chromium, molybdenum and vanadium will be treated in detail.

Copper is monovalent or divalent. Monovalent salts are called cuprous and the divalent salts are called cupric compounds.

Copper being low in the electromotive series; is rather inactive. Sometimes it is found free in nature, e.g., on the Michigan shore of Lake Superior. But the mine has been nearly exhausted and at present very little free copper exists there. One of its most important ores is chalcopyrite, $Cu_2S \cdot Fe_2S_3$. Copper pyrites, $CuFeS_2$, and Chalcocite, Cu_2S, are also valuable minerals. All these are sulfides. Malachite, $Cu_3(OH)_2CO_3$, and azurite, $Cu_3(OH)_2(CO_3)_2$, are basic carbonates. Cuprite, Cu_2O, is also an important ore.

There are two methods of recovering copper from the complex ores. The first, a thermal method, which is becoming less important each day, consists of roasting the ores and removing most of the sulfur as sulfur dioxide. The resulting material is introduced into a blast furnace along with some

unroasted ores, sand and coke. Here some of the iron is removed as a silicate slag. The resulting product, known as copper matte, is then bessemerized with sand in a converter to impure metallic copper, known as blister copper which contains some dissolved cuprous oxide. This is melted and stirred with clean wood and the carbon monoxide given off by the organic material reduces the cuprous oxide to the metallic state. In order to produce a very pure copper, which is essential for electrical work, it must be further purified by the electrolytic process, which consists of casting the copper into anodes and introducing it into a sulfuric acid copper sulfate solution and electrolyzing, using pure copper as the starting cathode. This produces a copper of 99.99% purity.

The second method, which is more important at the present time, consists of introducing the ore into large bins or containers, pouring sulfuric over the entire mass and allowing to filter through the ore. The sulfuric acid reacts with the complex copper salts producing copper sulfate. This solution is then taken to electrolytic tanks, using insoluble anodes and copper sheets as cathode. A current of thirty to sixty ampères per square foot is introduced and the copper ions in solution are reduced to metallic copper at the cathode. This produces a rather pure copper product in two operations. Copper melts at 1083°C and boils at 2300°C. The density of copper is 8.93 and it is very malleable and ductile. Copper does not unite with oxygen when both are perfectly dry. However, moist oxygen forms a thin film of cuprous oxide on the metal. Damp air forms a basic carbonate which is green. Copper does not displace hydrogen from dilute acids. However, oxygen acids attack the copper. Hydrochloric acid will also act on copper if oxygen is present.

$$2Cu + 4HCl + O_2 = 2CuCl_2 + 2H_2O$$

Copper is extensively used for conducting electricity. It is also used for electroplating, electrotyping, and making the following alloys: brass, bronze, bell metal, gun metal, barium, silver, and aluminum alloys.

Cuprous chloride, CuCl, may be made by boiling copper turnings, cupric chloride and hydrochloric acid together.

$$CuCl_2 + Cu = 2CuCl$$

Cuprous chloride is insoluble in water.

Red cuprous oxide, Cu_2O, can be formed by gently heating copper in air.

If sodium cyanide is added to the solution of a cupric salt, cupric cyanide, $Cu(CN)_2$, is precipitated. This salt decomposes to form cuprous cyanide.

$$2Cu(CN)_2 = 2CuCN + C_2N_2$$

Cyanogen, C_2N_2, is liberated as a gas. Cuprous cyanide is insoluble in water but is soluble in sodium cyanide solution, forming the double salt, sodium cuprocyanide, $NaCu(CN)_2$, which is used in the electroplating industry in large amounts.

$$NaCN + CuCN \rightarrow NaCu(CN)_2$$

There are many cupric salts but only the most important ones will be mentioned here. Cupric sulfate is formed by dissolving the oxide in sulfuric acid.

$$CuO + H_2SO_4 = CuSO_4 + H_2O$$

Copper sulfate crystallizes as the pentahydrate, $CuSO_4 \cdot 5H_2O$ This is also known as blue vitriol. If ammonium hydroxide is added to copper sulfate, a precipitate, the pale green basic

sulfate is produced. If excess hydroxide is now added, the complex compound, ammono-cupric sulfate, $Cu(NH_3)_4SO_4 \cdot H_2O$ results, which has a beautiful dark blue color. The formation of this complex is used as a test for copper. Cupric sulfate is used in large quantities to make up acid sulfate baths for electroplating, electrotyping, and electroforming of copper.

Cupric hydroxide, $Cu(OH)_2$, is a blue, gelatinous precipitate produced by adding sodium hydroxide to a soluble cupric salt.

$$CuSO_4 + 2NaOH = Cu(OH)_2 + Na_2SO_4$$

It is used as a spray on grape vines and other plants to prevent the growth of fungi.

Cupric oxide, CuO, is formed by heating copper in air or oxygen, or by igniting the nitrate.

Cupric nitrate, $Cu(NO_3)_2$, is obtained by treating copper with nitric acid.

$$8HNO_3 + 3Cu = 4H_2O + 2NO + 3Cu(NO_3)_2$$

It crystallizes out of solution with six molecules of water, $Cu(NO_3)_2 \cdot 6H_2O$.

Cupric cyanide cannot be precipitated from solution. If a soluble cupric salt is added to a cyanide solution, cuprous cyanide and cyanogen (a poisonous gas) is produced.

$$CuSO_4 + 2NaCN \rightarrow Na_2SO_4 + Cu(CN)_2$$
$$2Cu(CN)_2 \rightarrow 2CuCN + (CN)_2$$

All platers should become familiar with the above reactions, as cyanide baths are often made this way in the plating plant. If an excess of NaCN is added to the cuprous cyanide, the soluble complex is formed as has been pointed out above.

Cupric acetate is obtained by dissolving copper in acetic acid in the presence of oxygen.

$$6Cu + 8HC_2H_3O_2 + 3O_2 = 2Cu_3(OH)_2(C_2H_3O_2)_4 + 2H_2O$$

This is a basic acetate which dissolves in acetic acid from which normal copper acetate can be obtained.

Silver is found either in the native state or in the combined form. Most of the silver today occurs in the form of ores. There are three important silver ores, pyrargyrite, Ag_3SbS_3, proustite, Ag_3AsS_3, and horn silver, AgCl. It occurs in copper ores along with some gold. Most of our silver is obtained as a by-product from copper and lead ores. Pure silver is a white, crystalline metal melting at 960°C. Being very ductile, it can be drawn into very thin wires. It is used for silver plating, for making silverware, coins and alloys. Silver is not oxidized by oxygen but unites with sulfur to produce the black sulfide, Ag_2S. Silver does not displace hydrogen from acids but will react with the oxygen acids.

The chloride, bromide, and iodide of silver are all insoluble in water. They can be produced by adding a halide to a soluble silver salt.

$$AgNO_3 + NaCl = AgCl + NaNO_3$$

Silver, like copper, gives an insoluble silver cyanide, AgCN, and then forms, with excess cyanide, the complex salt, sodium argenticyanide, $NaAg(CN)_2$.

Silver nitrate, $AgNO_3$, is formed by the interaction of nitric acid and silver.

$$3Ag + 4HNO_3 = 3AgNO_3 + NO + 2H_2O$$

Gold is generally found in the free state encrusted in veins of quartz and also in some of the copper and lead ores. It is the most malleable and ductile metal. Gold melts at 1063°C. Copper, and sometimes nickel, is generally mixed with gold in order to increase its wearing qualities and the karat is used to denote the percentage gold present. Pure gold is of twenty-four karats. Gold is not affected by hydrogen sulfide, oxygen, or any acid, except selenic acid. It reacts, however, with aqua regia, a mixture of nitric and hydrochloric acids, giving chlorauric acid, $HAuCl_4$. Aqua regia dissolves gold because free chlorine is produced. Aurocyanides (e.g., $KAu(Cu)_2$) and auricyanides (e.g., $KAu(CN)_4$) are formed by the action of potassium cyanide on aurous and auric compounds. These salts are used in the electrodeposition of gold.

Platinum is a grayish-white metal, having a melting point of 1755°C. Being inactive, it is found in the free state in Russia, the United States, Africa, etc. It also occurs, in very small amounts, in copper ores. Platinum is used, to a great extent, for chemical apparatus in the laboratory. The oxygen acids do not affect platinum, neither do the alkali carbonates, but aqua regia dissolves it, forming chloroplatinic acid, H_2PtCl_6. It forms alloys with lead, antimony, and similar metals. If ammonium chloroplatinate, $(NH_4)_2PtCl_6$, is ignited, platinum sponge is produced. This form, due to its large surface, is used as a catalyst and also in electrical measuring instruments. Platinum is used as a catalyst in the contact method of making sulfuric acid and in the oxidation of ammonia. Platinum is also used in the jewelry industry.

Platinum forms soluble, complex phosphates which are used in the industry to deposit platinum.

Platinum is divalent or tetravalent. If chlorine is passed over finely divided platinum, which is heated to 250°C, platinous chloride, $PtCl_2$, is formed. It has a greenish color, is insoluble

in water, but will react with hydrochloric acid to form soluble chloroplatinous acid. A base precipitates platinous hydroxide, $Pt(OH)_2$, which is black. If this is heated, the oxide, PtO, is formed and heating to higher temperature will set the platinum free.

Platinocyanides can be formed by adding an alkali cyanide to the solution of a soluble platinum salt. The formula of potassium platinocyanide is $K_2Pt(CN)_4$.

Platinic chloride, $PtCl_4$, is formed by dissolving platinum in aqua regia to chloroplatinic acid, H_2PtCl_2, and passing a stream of chlorine over this solution which is heated to 360°C. Platinic hydroxide, $Pt(OH)_4$, is precipitated when bases are added to chloroplatinic acid. This compound is amphoteric, that is, it reacts with either acids or bases.

Rhodium is not attacked by aqua regia, but reacts with chlorine. It is harder than platinum and is used to form platinum alloys which are harder than the original platinum. Rhodium is found in complex copper and nickel ores and is a by-product of copper and nickel manufacture. It forms complex amines and phosphates, both of which are used in electroplating baths.

Palladium is similar to platinum in many respects. It was not used very much for plating until the present war. It dissolves in nitric acid, and forms complex cyanides and amines. The complex phosphates seem to give the best electrodeposits. One of the most interesting properties of palladium is its ability to absorb large volumes of hydrogen. One volume of palladium can absorb 800–900 volumes of hydrogen. Palladium is not attacked by sulfides, oxygen, or moisture. It is used as a catalyst.

Chromium is a very important metal in the electroplating and steel-alloying industries. It is not found in nature as a metal, due to its activity, but it is generally mined as chromite,

$Fe(CrO_2)_2$, in Rhodesia and New Caledonia. The metal can be obtained from the oxide by reducing with carbon in an electric furnace.

Chromium is a silvery-blue metal, very hard, having a melting point of 1520°C and a density of 6.9. Nitric acid does not attack chromium. It is readily soluble in hydrochloric acid. Chromium is divalent, trivalent or hexavalent.

Chromous chloride, $CrCl_2$, is formed by dissolving chromium in hydrochloric acid.

$$Cr + 2HCl \rightarrow CrCl_2 + H_2$$

Chromic chloride, $CrCl_3$, can be made as follows:

$$2CrO_3 + 6HCl + \underset{\text{ethyl alcohol}}{3C_2H_5OH} \rightarrow 2CrCl_3 + \underset{\text{acetaldehyde}}{3C_2H_4O} + 6H_2O$$

Here the ethyl alcohol is oxidized to acetaldehyde. $CrCl_3$ can also be formed by the reaction of HCl on $Cr(OH)_3$.

$$Cr(OH)_3 + 3HCl \rightarrow CrCl_3 + 3H_2O$$

If chromite is heated to 1000°C in air with sodium carbonate, soluble sodium chromate is produced.

$$4Fe(CrO_2)_2 + 7O_2 + 8Na_2CO_3 \rightarrow 2Fe_2O_3 + 8CO_2 + 8Na_2CrO_4$$

If potassium chromate is acidified with sulfuric acid, potassium dichromate, $K_2Cr_2O_7$, results.

$$2K_2CrO_4 + H_2SO_4 = K_2Cr_2O_7 + H_2O + K_2SO_4$$

Chromium trioxide or chromic anhydride, CrO_3, when dissolved in water, forms chromic acid. Chromium anhydride

is made by adding concentrated sulfuric acid to a chromate or dichromate.

$$Na_2Cr_2O_7 + H_2SO_4 = Na_2SO_4 + H_2O + 2CrO_3$$

Chromium trioxide is used as an oxidizing agent and for forming a chromium-plating bath. If heated, it loses oxygen and forms the green chromic oxide.

$$4CrO_3 = 2Cr_2O_3 + 3O_2$$

Chromous hydroxide, $Cr(OH)_2$, can be prepared as a yellow precipitate by adding a base to chromous chloride.

Chromic hydroxide is prepared as a pale blue precipitate by adding ammonium hydroxide to a chromic salt. Its formula is $2Cr(OH)_3 \cdot H_2O$. It is very unstable.

There are two important ores of tungsten, wolframite, $(FeMn)WO_4$, and scheelite, $CaWO_4$. It has the highest melting point of all metals, melting at 3370°C. It is very heavy and hard and has a steel gray color. Tungsten does not oxidize in air and is not attacked by cold acids. It exhibits a valence of two, four, five, and six, and forms chlorides, oxides, and tungstates. One of the most important uses of tungsten is as a filament in electric bulbs. It is also used in making high-speed steels and other steel alloys.

Molybdenum occurs as molybdenite, MoS_2, which is a black, finely-powdered mineral resembling graphite, but being much heavier. Molybdenum is a silvery-white metal, melting at 2500°C. Its principal use is for making ferro alloys. If MoS_2 is roasted, MoO_3 is formed. This can be dissolved in sodium hydroxide to produce sodium molybdate, Na_2MoO_4.

Vanadium is a silvery-white, rather hard metal. There are

no special uses for the metal as such, but vanadium-ferric alloys are in demand because of their hardness and tensile strength. It melts at 1720°C. The oxide of vanadium is used as a catalyst.

QUESTIONS

1. Why does silver tarnish? Write the equation.
2. Write the equation for the reaction which occurs when iron is introduced into a copper sulfate solution.
3. How does a plater prevent the above from taking place in the plant?
4. Write the equation for the interaction of cuprous cyanide with potassium cyanide.
5. Give a use for platinum in the plating industry.
6. Why is chromium plated from the hexavalent state instead of the trivalent state?
7. What compound is used to produce chromium ions in a plating bath?
8. Why is gold plating desired in many instances?
9. How many grams of silver nitrate can be obtained from 100 grams of silver?
10. 25 cc of a 0.1 normal solution of HCl neutralize 10 cc of an unknown sodium hydroxide solution. What is the normality of the sodium hydroxide solution?

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